

## Supporting Information

### An efficient synthesis of 2-CF<sub>3</sub>-3-benzylindoles

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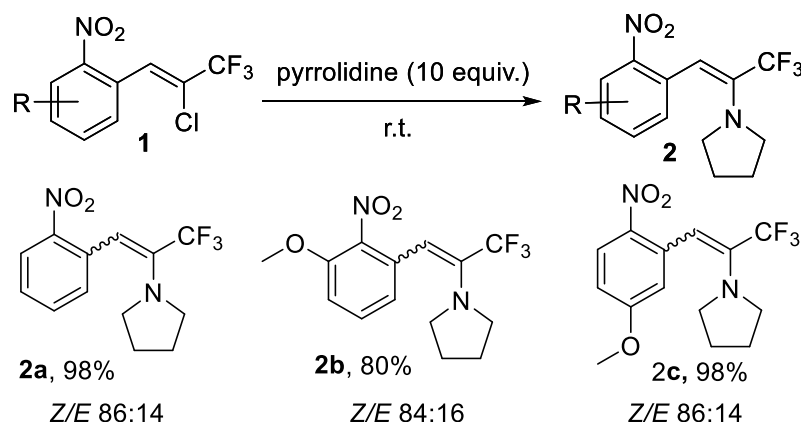
#### Table of contents

|   |                |
|---|----------------|
| <b>General remarks</b>  | <b>S2</b>      |
| <b>Synthesis of <math>\alpha</math>-CF<sub>3</sub>-<math>\beta</math>-(2-nitroaryl)enamines <b>2</b> by the reaction with pyrrolidine in neat (general procedure)</b> | <b>S2</b>      |
| <b>Synthesis of ketones <b>3</b> by the reactions of <math>\alpha</math>-(trifluoromethyl)enamines with aromatic aldehydes (general procedure)</b>                    | <b>S3</b>      |
| <b>Reductive cyclization of nitro-ketone <b>3a</b> to 2-CF<sub>3</sub>-indoles in various conditions (a-h)</b>  | <b>S4-S6</b>   |
| <b>Reductive cyclization of nitro-ketones <b>3</b> to 2-CF<sub>3</sub>-indoles <b>4</b></b>   | <b>S7-S14</b>  |
| <b>NMR data of the reaction intermediates</b>   | <b>S15</b>     |
| <b>Copies of all NMR spectra</b>  | <b>S16-S95</b> |

## Experimental section

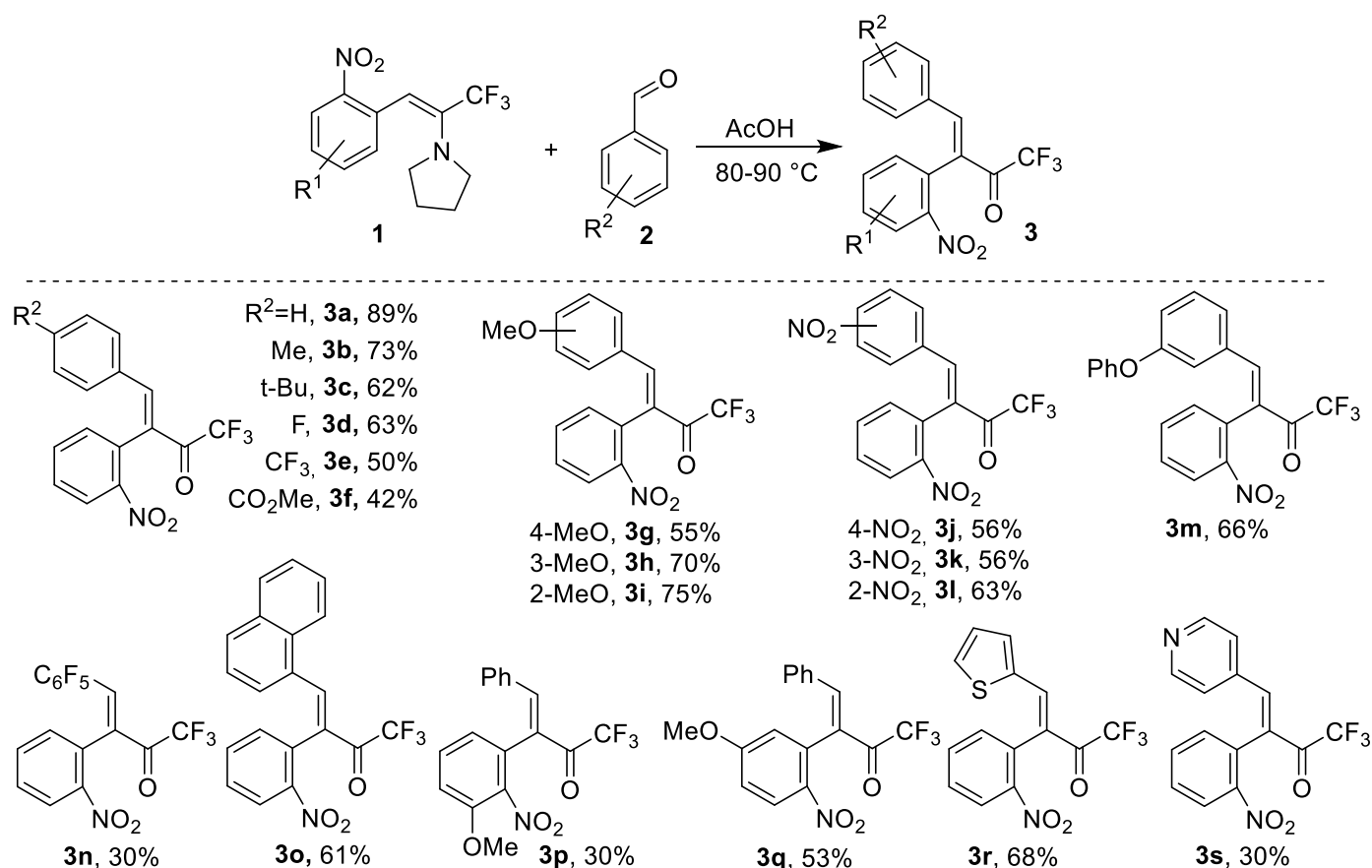
**General remarks.**  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were recorded on Bruker AVANCE 400 MHz spectrometer in  $\text{CD}_3\text{CN}$  and  $\text{CDCl}_3$  at 400, 100 and 376 MHz respectively. Chemical shifts ( $\delta$ ) in ppm are reported with the use of the residual  $\text{CHD}_2\text{CN}$  and chloroform signals (1.94 and 7.25 for  $^1\text{H}$  and 1.30, 77.0 for  $^{13}\text{C}$ ) as internal reference. The  $^{19}\text{F}$  chemical shifts were referenced to  $\text{C}_6\text{F}_6$ , (-162.9 ppm). ESI-MS spectra were measured with an Orbitrap Elite instrument. TLC analysis was performed on “Merck 60  $\text{F}_{254}$ ” plates. Column chromatography was performed on silica gel. Melting points were determined on an Electrothermal 9100 apparatus. All reagents were of reagent grade and were used as such or were distilled prior to use. Starting  $\alpha$ - $\text{CF}_3$ - $\beta$ -aryl enamines **1** were synthesized using previously reported procedures by the reaction with 10 equivalents of pyrrolidine in neat. [1. Muzalevskiy, V. M.; Nenajdenko, V. G.; Rulev, A. Yu.; Ushakov, I. A.; Romanenko, G. V.; Shastin, A. V.; Balenkova, E. S.; Haufe, G. Selective synthesis of  $\alpha$ -trifluoromethyl- $\beta$ -arylenamines or vinylogous guanidinium salts by treatment of  $\beta$ -halo- $\beta$ -trifluoromethylstyrenes with secondary amines under different conditions. *Tetrahedron* **2009**, 65 (34), 6991 - 7000.]

**Synthesis of  $\alpha$ - $\text{CF}_3$ - $\beta$ -(2-nitroaryl)enamines **1** by the reaction with pyrrolidine in neat (general procedure).** A one neck 25 mL round bottomed flask was charged with dry pyrrolidine (8.5 mL, 100 mmol), cooled down to  $-18\text{ }^\circ\text{C}$  and the corresponding styrene (10 mmol) was added in one portion with vigorous stirring. The reaction mixture was stirred at room temperature for 1-3 h until starting styrene was consumed (TLC or NMR monitoring). The excess of pyrrolidine was evaporated in vacuum, the viscous residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL), washed with 10%  $\text{K}_2\text{CO}_3$  solution ( $2 \times 50\text{ mL}$ ) and dried over  $\text{Na}_2\text{SO}_4$ .  $\text{CH}_2\text{Cl}_2$  was removed in vacuo to give crude enamine, which was used without further purification. For characterization data of enamines **1** see [2] (Muzalevskiy, V. M.; Sizova, Z. A.; Nenajdenko, V. G. Modular Construction of Functionalized 2- $\text{CF}_3$ -Indoles. *Org. Lett.*, **2021**, ASAP, DOI: 10.1021/acs.orglett.1c02061).



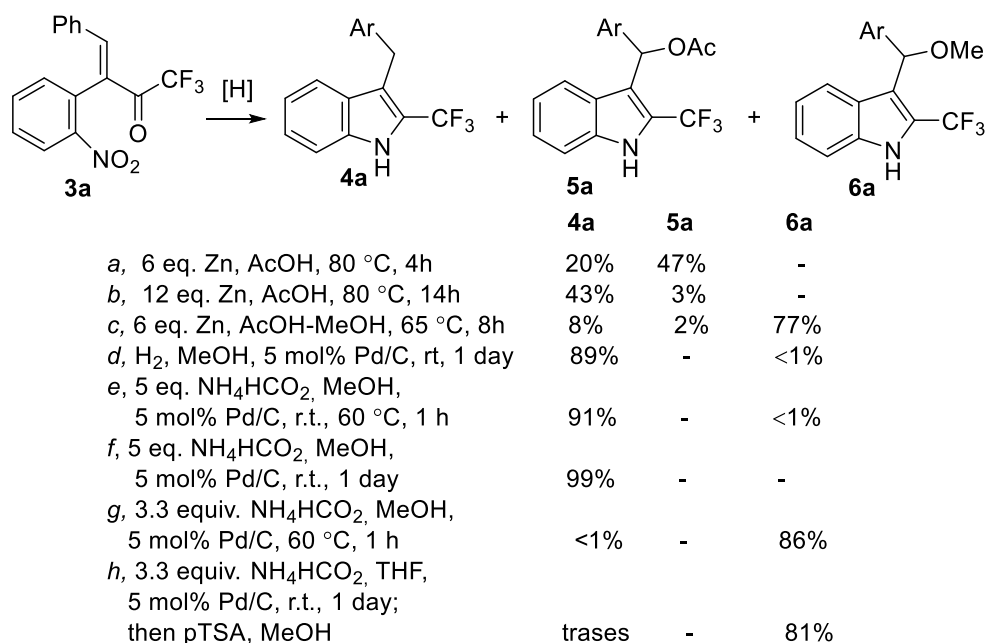
Scheme S1. Synthesis of  $\text{CF}_3$ -enamines **1**.

**Synthesis of ketones **3** by the reactions of  $\alpha$ -(trifluoromethyl)enamines with aromatic aldehydes (general procedure).** One-necked 50-mL round bottom flask (or 12 mL vial) was charged with enamine **1** (5 mmol), aromatic aldehyde **2** (5.75 mmol) and glacial acetic acid (15 mL or 5 mL for reaction in vial). Reaction mixture was kept at 80-90 °C (hotplate stirrer) under stirring for 6-10 hours until consumption of aldehyde and corresponding benzyl ketone formed by the hydrolysis of enamine ( $^1\text{H}$  NMR control). Volatiles were evaporated in vacuo, the residue was dissolved in  $\text{CH}_2\text{Cl}_2$  (50 mL), washed with water (2×20 mL) and dried over  $\text{Na}_2\text{SO}_4$ . Volatiles were evaporated Please confirm if this should be deleted., the residue was purified by column chromatography, using mixtures of hexane and  $\text{CH}_2\text{Cl}_2$  (3:1, 1:1),  $\text{CH}_2\text{Cl}_2$ , mixture of  $\text{CH}_2\text{Cl}_2$  and MeOH (100:1) as eluents. For characterization data of ketones **3** see [2] (Muzalevskiy, V. M.; Sizova, Z. A.; Nenajdenko, V. G. Modular Construction of Functionalized 2- $\text{CF}_3$ -Indoles. *Org. Lett.*, **2021**, ASAP, DOI: 10.1021/acs.orglett.1c02061).



Scheme S2.

## Reductive cyclization of nitro-ketone **3a** to 2-CF<sub>3</sub>-indoles in various conditions (a-h)



Scheme S3.

**Conditions (a,b), Zn in AcOH.** 12 mL vial with a screw cap was charged with ketone **3a** (0.0551 g, 0.172 mmol), Zn (0.067 g, 1.03 mmol, 6 equiv.) and AcOH (2 mL). Next, the reaction mixture was kept at 80 °C (hotplate stirrer) under stirring for 4 hours.\* The reaction mixture was dispersed between water (10-15 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). Combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, volatiles were evaporated in vacuo, and passed through a short sicagel pad, using mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) as an eluent. Evaporation of the solvents gave a mixture of indoles **4a** and **5a**. Conditions a: for the mixture of **4a** and **5a**: brown oil, 0.036 g, yield of **5a** - 47%, yield of **4a** - 20%. For characterization data of **4a** and **5a** see below. Conditions b: for the mixture of **4a** and **5a**: brown oil, 0.025 g, yield of **5a** - 3%, yield of **4a** - 43%.

\*-In case of conditions **b** at that point additional amount of Zn (0.067 g, 1.03 mmol, 6 equiv.) was added and the reaction mixture was kept at 80 °C (hotplate stirrer) under stirring for another 10 hours

**Phenyl(2-(trifluoromethyl)-1H-indol-3-yl)methyl acetate (5a).** Pale brown solid, m.p. 48-50 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.55 (br.s, 1H), 7.70 (d, 1H, <sup>3</sup>J = 8.2 Hz), 7.43 (s, 1H), 7.36-7.42 (m, 3H), 7.24-7.34 (m, 4H), 7.09-7.16 (m, 1H), 2.17 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 170.0, 139.2, 135.2, 128.4, 127.9, 126.5, 125.6, 125.0, 122.4 (q, <sup>2</sup>J<sub>CF</sub> = 37.9 Hz), 122.1, 121.4 (q, <sup>1</sup>J<sub>CF</sub> = 268.9 Hz), 121.3, 116.1 (q, <sup>3</sup>J<sub>CF</sub> = 2.5 Hz), 111.9, 70.0, 21.0. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.0 (s, 3F). HRMS (ESI-TOF): m/z [M-Ac]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>12</sub>F<sub>3</sub>NO: 290.0798; found: 290.0797.

**Conditions (c), Zn in AcOH-MeOH.** 12 mL vial with a screw cap was charged with ketone **3a** (0.0482 g, 0.15 mmol), Zn (0.059 g, 0.9 mmol, 6 equiv.), AcOH (1 mL) and MeOH (1 mL). Next, the reaction mixture was kept at 65 °C (hotplate stirrer) under stirring for 8 hours. The reaction mixture was dispersed between water (10-15 mL) and CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). Combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, volatiles were evaporated in vacuo, and passed through a short sicagel pad, using mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) as an eluent. Evaporation of the solvents gave a mixture of indoles **4a**, **5a** and **6a**. For the mixture of **4a**, **5a** and **6a**: brown oil, 0.039 g, yield of **5a** - 2%, yield of **4a** - 8%, yield of **6a** - 77%. For characterization data of **4a**, **5a** and **6a** see below.

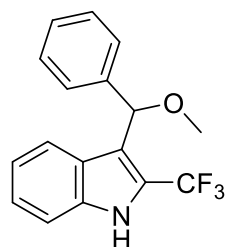
**Conditions (d), H<sub>2</sub> in MeOH (on Pd/C).** 25 mL three-neck round bottom flask equipped with two glass stop corks, and gas inlet was charged with ketone **3a** (0.095 g, 0.3 mmol), Pd/C (10%, 0.013 g, 0.012 mmol, 5 mol%), methanol (5 mL) and evacuated in vacuo. A balloon with hydrogen was connected to the gas inlet and the flask was filled with hydrogen. The reaction mixture was magnetically stirred for 1 day, the hydrogen balloon was disconnected, the flask was evacuated in vacuo through gas inlet and filled carefully with air. The reaction mixture filtered through celite, volatiles were evaporated in vacuo, the residue was purified by column chromatography, using mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> (3:1) as an eluent. Evaporation of the solvents afforded indole **4a** as a pale brown solid, yield 0.0735 g (89%). For characterization data of **4a** see below.

**Conditions (e), NH<sub>4</sub>HCO<sub>2</sub> (5 equiv.) in MeOH, Pd/C (10%), 60 °C.** 12 mL vial with a screw cap was charged with ketone **3a** (0.108 g, 0.336 mmol), NH<sub>4</sub>HCO<sub>2</sub> (0.105 g, 1.67 mmol, 5 equiv.), Pd/C (10%, 0.016 g, 0.015 mmol, 5 mol%) and methanol (1 mL). Next, the reaction mixture was kept at 60 °C (hotplate stirrer) under stirring at room temperature for 1 h. After that, 6M HCl (0.3 mL, 1.8 mmol) was added in 4-5 portions (evolution of CO<sub>2</sub>!). The reaction mixture was filtered through a short celite pad and dispersed between water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). Combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, volatiles were evaporated in vacuo, to give pure indole **4a**. Pale brown crystals. For characterization data of **4a** see below.

**Conditions (f), NH<sub>4</sub>HCO<sub>2</sub> (5 equiv.) in MeOH, Pd/C (10%).** 12 mL vial with a screw cap was charged with ketone **3a** (0.055 g, 0.171 mmol), NH<sub>4</sub>HCO<sub>2</sub> (0.49 g, 0.78 mmol, 5 equiv.), Pd/C (10%, 0.009 g, 0.085 mmol, 5 mol%) and methanol (1 mL). Next, the reaction mixture was kept under stirring at room temperature for 1 day.\* After that, 6M HCl (0.25 mL, 1.5 mmol) was added in 4-5 portions (evolution of CO<sub>2</sub>!). The reaction mixture was filtered through a short celite pad and dispersed between water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). Combined organic phases were

dried over Na<sub>2</sub>SO<sub>4</sub>, volatiles were evaporated in vacuo, to give pure indole **4a**. \*-Evaporation of MeOH at this step afforded crude indolinol **D** as a mixture with indole **6** 2:1. Pale brown oil. For NMR data see below.

**Conditions (g), NH<sub>4</sub>HCO<sub>2</sub> (3.3 equiv.) in MeOH, Pd/C (10%).** 12 mL vial with a screw cap was charged with ketone **3a** (0.055 g, 0.171 mmol), NH<sub>4</sub>HCO<sub>2</sub> (0.036 g, 0.571 mmol, 3.3 equiv.), Pd/C (10%, 0.009 g, 0.084 mmol, 5 mol%) and methanol (1 mL). Next, the reaction mixture was kept under stirring at room temperature for 1 day. After that, 6M HCl (0.25 mL, 1.5 mmol) was added in 4-5 portions (evolution of CO<sub>2</sub>!). The reaction mixture was filtered through a short celite pad and dispersed between water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). Combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, volatiles were evaporated in vacuo, the residue was purified by column chromatography, using mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> (3:1) as eluent. Evaporation of the solvents afforded indole **6a** as a slightly brown solid, m.p. 86-88 °C, yield 0.045 g (86%).

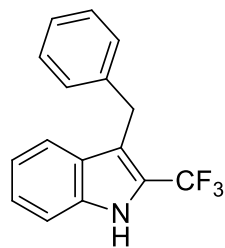


**3-(Methoxy(phenyl)methyl)-2-(trifluoromethyl)-1H-indole (6a).** <sup>1</sup>H NMR

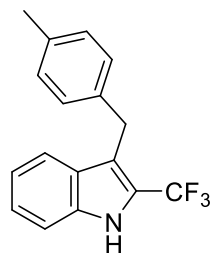
(CDCl<sub>3</sub>, 400.1 MHz): δ 8.40 (br.s, 1H), 7.79 (d, 1H, <sup>3</sup>J = 8.2 Hz), 7.49 (d, 2H, <sup>3</sup>J = 7.4 Hz), 7.26-7.39 (m, 4H), 7.20-7.25 (m, 1H), 7.06-7.13 (m, 1H), 5.83 (s, 1H), 3.42 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 141.3, 135.4, 128.2, 127.2, 126.4, 125.4, 124.9, 123.0 (q, <sup>2</sup>J<sub>CF</sub> = 37.0 Hz), 122.9, 121.8 (q, <sup>1</sup>J<sub>CF</sub> = 269.2 Hz), 121.0, 117.9 (q, <sup>3</sup>J<sub>CF</sub> = 2.6 Hz), 111.6, 77.5, 56.9. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -58.2 (s, 3F). HRMS (ESI-TOF): m/z [M-H]<sup>-</sup> Calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>-</sup>: 304.0955; found: 304.0945.

**Conditions (h) NH<sub>4</sub>HCO<sub>2</sub> (3.3 equiv.) in MeOH, Pd/C (10%). 1) Preparation of solution of indolinol B.** 20 mL vial with a screw cap was charged with ketone **3a** (0.963 g, 3 mmol), NH<sub>4</sub>HCO<sub>2</sub> (0.623 g, 9.9 mmol, 3.3 equiv.), Pd/C (10%, 0.162 g, 0.15 mmol, 5 mol%) and THF (12 mL). Next, the reaction mixture was kept under stirring at room temperature for about 1 day (20 h, <sup>19</sup>F NMR control). The reaction mixture was filtered through a short celite pad, celite was washed with THF (3×2 mL) to obtain 9.47 g of solution of **B** (0.1 mmol of **B** in approximately 0.316 g of the solution). Evaporation of THF led to a crude indolinol **B** as a light yellow-green solid, m.p. 50-55 °C. For NMR data see below. **2) Reaction with MeOH under p-TSA×H<sub>2</sub>O catalysis.** 12 mL vial with a screw cap was charged with solution of **B** (0.632 g, ~0.2 mmol), MeOH (0.200 g, 6.25 mmol), stirred for 5 minutes and then *p*-TSA (0.038 g, 0.2 mmol, 1 equiv.) was added. The reaction mixture was stirred overnight, volatiles were evaporated in vacuo, the residue was purified by column chromatography, using mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> (3:1) as an eluent. Evaporation of the solvents afforded indole **6a** as a slightly brown solid, yield 0.049 g (81%).

**Reductive cyclization of nitro-ketones 3 to 2-CF<sub>3</sub>-indoles 4.** 12 mL vial with a screw cap was charged with ketone **4** (0.2 mmol), NH<sub>4</sub>HCO<sub>2</sub> (0.063 g, 1.00 mmol, 5 equiv.), Pd/C (10%, 0.0108 g, 0.01 mmol, 5 mol%) and methanol (1.2 mL). Next, the reaction mixture was kept under stirring at 60 °C for 0.5-1 h (conditions A) or at room temperature for 1 day (conditions B). After that, 6M HCl (0.25 mL, 1.5 mmol) was added in 4-5 portions (evolution of CO<sub>2</sub>!). The reaction mixture was filtered through a short celite pad and dispersed between water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). Combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, volatiles were evaporated in vacuo, to give pure indole **4**. In case of indoles **4l**, **4n**, **4r**, **4s** additional purification by column chromatography on silica gel was performed. Reduction of ketones **3j-l**, having additional nitro group, was performed using 8 equivalents of NH<sub>4</sub>HCO<sub>2</sub> at room temperature (conditions C).

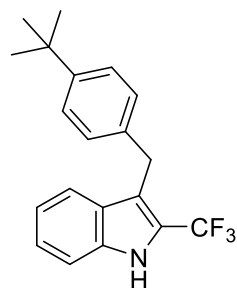


**3-Benzyl-2-(trifluoromethyl)-1H-indole (4a).** Obtained using conditions A (0.108 g, 0.34 mmol of **3a**) or conditions B (0.055 g, 0.171 mmol of **3a**). Pale brown crystals, m.p. 103-104 °C, yield 0.084 g (91%, A) 0.0465 g (99%, B). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.25 (br.s, 1H), 7.57 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.39 (d, 1H, <sup>3</sup>J = 8.2 Hz), 7.27-7.37 (m, 5H), 7.20-7.26 (m, 1H), 7.13-7.19 (m, 1H), 4.32 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 139.9, 135.3, 128.4, 128.3, 127.4, 126.1, 124.8, 122.03 (q, <sup>2</sup>J<sub>CF</sub> = 36.5 Hz), 122.01 (q, <sup>1</sup>J<sub>CF</sub> = 269.0 Hz), 120.8, 120.7, 116.8 (q, <sup>3</sup>J<sub>CF</sub> = 2.8 Hz), 111.7, 29.8. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.1 (s, 3F). NMR data are in agreement with those in the literature [3. Cheng, Y., Yuan, X., Ma, J. and Yu, S. Direct Aromatic C-H Trifluoromethylation via an Electron-Donor–Acceptor Complex. *Chem. Eur. J.*, **2015**, *21*, 8355-8359.]

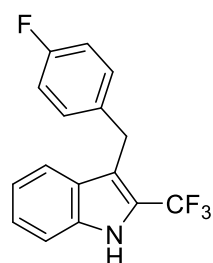


**3-(4-Methylbenzyl)-2-(trifluoromethyl)-1H-indole (4b).** Obtained using conditions A (0.109 g, 0.325 mmol of **3b**). Pale brown solid, m.p. 88-90 °C, yield 0.090 g (96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.24 (br.s, 1H), 7.63 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.35-7.44 (m, 2H), 7.25 (d, 2H, <sup>3</sup>J = 8.0 Hz), 7.19-7.23 (m, 1H), 7.17 (d, 2H, <sup>3</sup>J = 7.9 Hz), 4.33 (s, 2H), 2.39 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 136.9, 135.6, 135.3, 129.1, 128.1, 127.4, 124.7, 122.1 (q, <sup>1</sup>J<sub>CF</sub> = 269.0 Hz), 121.9 (q, <sup>2</sup>J<sub>CF</sub> = 36.5 Hz), 120.8, 120.6, 117.0 (q, <sup>3</sup>J<sub>CF</sub> = 2.8 Hz), 111.6, 29.3, 20.9. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.1 (s, 3F). HRMS (ESI-TOF): m/z [M-H]<sup>-</sup> Calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>N: 288.1006; found: 288.1009.

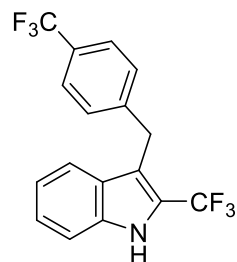
C17H14F3N



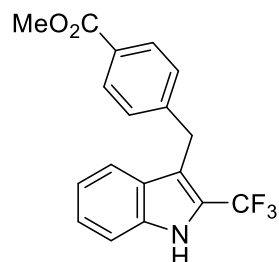
**3-(4-(*tert*-Butyl)benzyl)-2-(trifluoromethyl)-1H-indole (4c).** Obtained using conditions B (0.120 g, 0.318 mmol of **3c**). Pale brown solid, m.p. 85-87 °C, yield 0.100 g (95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.23 (br.s, 1H), 7.64 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.33-7.42 (m, 4H), 7.25-7.32 (m, 2H), 7.19 (ddd, 1H, <sup>3</sup>J = 8.0 Hz, <sup>3</sup>J = 6.6 Hz, <sup>4</sup>J = 1.4 Hz), 4.32 (s, 2H), 1.36 (s, 9H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 148.9, 136.9, 135.3, 127.9, 127.5, 125.3, 124.8, 122.0 (q, <sup>1</sup>J<sub>CF</sub> = 269.1 Hz), 121.9 (q, <sup>2</sup>J<sub>CF</sub> = 36.7 Hz), 120.9, 120.6, 117.1 (q, <sup>3</sup>J<sub>CF</sub> = 2.6 Hz), 111.6, 34.3, 31.3, 29.2. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.0 (s, 3F). HRMS (ESI-TOF): m/z [M-H]<sup>-</sup> Calcd for C<sub>20</sub>H<sub>19</sub>F<sub>3</sub>N<sup>-</sup>: 330.1475; found: 330.1472.



**3-(4-Fluorobenzyl)-2-(trifluoromethyl)-1H-indole (4d).** Obtained using conditions A (0.126 g, 0.372 mmol of **3d**). Brown viscous oil, yield 0.105 g (96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.30 (br.s, 1H), 7.56 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.33-7.45 (m, 2H), 7.16-7.28 (m, 3H), 6.94-7.05 (m, 2H), 4.29 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 161.3 (d, <sup>1</sup>J<sub>CF</sub> = 243.8 Hz), 135.6 (d, <sup>4</sup>J<sub>CF</sub> = 2.8 Hz), 135.3, 129.6 (d, <sup>3</sup>J<sub>CF</sub> = 7.9 Hz), 127.3, 124.9, 122.0 (q, <sup>2</sup>J<sub>CF</sub> = 36.4 Hz), 121.9 (q, <sup>1</sup>J<sub>CF</sub> = 269.0 Hz), 120.8, 120.6, 116.6 (q, <sup>3</sup>J<sub>CF</sub> = 2.6 Hz), 115.1 (d, <sup>2</sup>J<sub>CF</sub> = 21.3 Hz), 111.7, 28.9. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.1 (s, 3F), -118.19 - -118.55 (m, 1F). HRMS (ESI-TOF): m/z [M-H]<sup>-</sup> Calcd for C<sub>16</sub>H<sub>10</sub>F<sub>4</sub>N<sup>-</sup>: 292.0755; found: 292.0749.



**2-(Trifluoromethyl)-3-(4-(trifluoromethyl)benzyl)-1H-indole (4e).** Obtained using conditions B (0.147 g, 0.378 mmol of **3e**). Pale brown solid, m.p. 54-56 °C, yield 0.129 g (>99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.36 (br.s, 1H), 7.50-7.66 (m, 3H), 7.40-7.49 (m, 1H), 7.39-7.40 (m, 3H), 7.19 (t, 1H, <sup>3</sup>J = 7.5 Hz), 4.35 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 144.0, 135.3, 128.49 (q, <sup>2</sup>J<sub>CF</sub> = 32.3 Hz), 128.51, 127.2, 125.4 (q, <sup>3</sup>J<sub>CF</sub> = 3.7 Hz), 124.3 (q, <sup>1</sup>J<sub>CF</sub> = 271.9 Hz), 122.4 (q, <sup>2</sup>J<sub>CF</sub> = 36.8 Hz), 121.9 (q, <sup>1</sup>J<sub>CF</sub> = 269.1 Hz), 121.0, 120.4, 115.6 (q, <sup>3</sup>J<sub>CF</sub> = 2.6 Hz), 111.9, 29.5. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.1 (s, 3F), -63.4 (s, 3F). HRMS (ESI-TOF): m/z [M-H]<sup>-</sup> Calcd for C<sub>17</sub>H<sub>10</sub>F<sub>6</sub>N<sup>-</sup>: 342.0723; found: 342.0714.

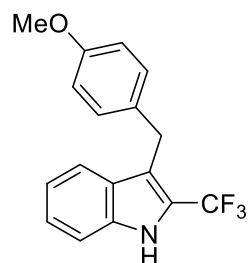


**Methyl 4-((2-(trifluoromethyl)-1H-indol-3-yl)methyl)benzoate (4f).** Obtained using conditions B (0.085 g, 0.224 mmol of **3f**). Pale yellow solid, m.p. 109-111 °C, yield 0.074 g (>99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.69 (br.s, 1H), 7.95 (d, 2H, <sup>3</sup>J = 8.3 Hz), 7.48 (d, 2H, <sup>3</sup>J = 8.1 Hz), 7.41 (d, 1H, <sup>3</sup>J = 8.3 Hz), 7.27-7.35 (m, 3H), 7.10-7.16 (m, 1H), 4.32 (s, 2H), 3.90 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 167.2, 145.5, 135.4, 129.8, 128.3, 128.0, 127.2, 124.9, 122.3 (q, <sup>2</sup>J<sub>CF</sub> = 36.8 Hz), 121.9 (q,



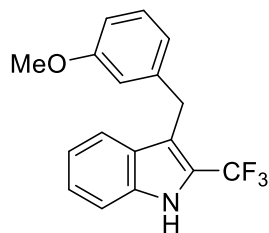
$^1J_{\text{CF}} = 269.0$  Hz), 120.8, 120.4, 115.5 (q,  $^3J_{\text{CF}} = 2.9$  Hz), 111.8, 52.0, 29.8.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -59.1 (s, 3F). HRMS (ESI-TOF):  $m/z$   $[\text{M}-\text{H}]^-$  Calcd for  $\text{C}_{18}\text{H}_{13}\text{F}_3\text{NO}_2^-$ : 332.0904; found: 332.0904.

**3-(4-Methoxybenzyl)-2-(trifluoromethyl)-1H-indole (4g).** Obtained using conditions B (0.057 g,



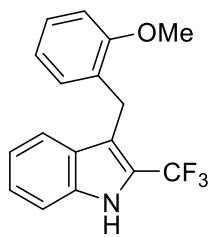
0.161 mmol of **3g**). White powder, m.p. 116-118 °C, yield 0.047 g (95%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  8.34 (br.s, 1H), 7.56 (d, 1H,  $^3J = 8.1$  Hz), 7.37 (d, 1H,  $^3J = 8.2$  Hz), 7.32 (t, 1H,  $^3J = 7.5$  Hz), 7.20 (d, 2H,  $^3J = 8.5$  Hz), 7.11-7.17 (m, 1H), 6.84 (d, 2H,  $^3J = 8.6$  Hz), 4.24 (s, 2H), 3.79 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  157.8, 135.3, 132.1, 129.2, 127.4, 124.8, 122.0 (q,  $^1J_{\text{CF}} = 268.9$  Hz), 121.9 (q,  $^2J_{\text{CF}} = 36.7$  Hz), 120.8, 120.6, 117.2 (q,  $^3J_{\text{CF}} = 2.8$  Hz), 113.8, 111.7, 55.2, 28.9.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -59.1 (s, 3F). HRMS (ESI-TOF):  $m/z$   $[\text{M}-\text{H}]^-$  Calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}^-$ : 304.0955; found: 304.0945.

**3-(3-Methoxybenzyl)-2-(trifluoromethyl)-1H-indole (4h).** Obtained using conditions B (0.104 g,



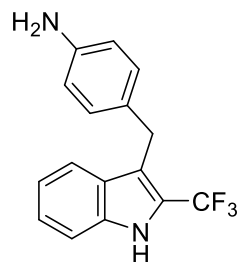
0.296 mmol of **3h**). Pale brown solid, m.p. 55-57 °C, yield 0.080 g (89%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  8.35 (br.s, 1H), 7.57 (d, 1H,  $^3J = 8.1$  Hz), 7.28-7.38 (m, 2H), 7.21 (d, 1H,  $^3J = 7.9$  Hz), 7.12-7.17 (m, 1H), 6.90 (d, 1H,  $^3J = 7.7$  Hz), 6.85 (*pseudo*-s, 1H), 6.77 (dd, 1H,  $^3J = 8.2$  Hz,  $^4J = 2.3$  Hz), 4.28 (s, 2H), 3.77 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  159.6, 141.6, 135.3, 129.3, 127.4, 124.8, 122.01 (q,  $^2J_{\text{CF}} = 36.5$  Hz), 121.99 (q,  $^1J_{\text{CF}} = 269.1$  Hz), 120.8, 120.70, 120.65, 116.5 (q,  $^3J_{\text{CF}} = 2.9$  Hz), 114.3, 111.7, 111.2, 55.0, 29.7.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -59.0 (s, 3F). HRMS (ESI-TOF):  $m/z$   $[\text{M}-\text{H}]^-$  Calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}^-$ : 304.0955; found: 304.0953.

**3-(2-Methoxybenzyl)-2-(trifluoromethyl)-1H-indole (4i).** Obtained using conditions B (0.116 g,



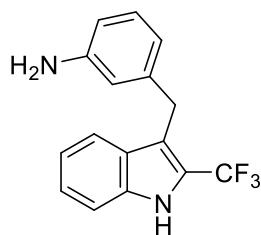
0.330 mmol of **3i**). Pale yellow solid, m.p. 67-69 °C, yield 0.099 g (98%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  8.28 (br.s, 1H), 7.58 (d, 1H,  $^3J = 8.1$  Hz), 7.31-7.41 (m, 2H), 7.20-7.25 (m, 1H), 7.15 (ddd, 1H,  $^3J = 8.0$  Hz,  $^3J = 6.8$  Hz,  $^4J = 1.2$  Hz), 6.96-7.02 (m, 1H), 6.94 (dd, 1H,  $^3J = 8.2$  Hz,  $^4J = 0.7$  Hz), 6.85 (td, 1H,  $^3J = 7.5$  Hz,  $^4J = 1.0$  Hz), 4.34 (s, 2H), 3.94 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  157.0, 135.3, 129.2, 128.2, 127.7, 127.2, 124.7 122.3 (q,  $^2J_{\text{CF}} = 36.7$  Hz), 122.1 (q,  $^1J_{\text{CF}} = 269.0$  Hz), 121.0, 120.5, 120.4, 116.5 (q,  $^3J_{\text{CF}} = 2.7$  Hz), 111.5, 109.9, 55.2, 23.3.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -59.3 (s, 3F). HRMS (ESI-TOF):  $m/z$   $[\text{M}-\text{H}]^-$  Calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_3\text{NO}^-$ : 304.0955; found: 304.0951.

**4-((2-(Trifluoromethyl)-1H-indol-3-yl)methyl)aniline (4j).** Obtained using conditions C (0.112 g,



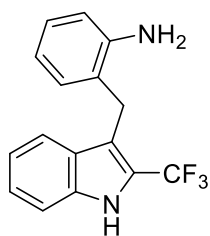
0.306 mmol of **3j**). Pale brown solid, m.p. 175-177 °C, yield 0.087 g (98%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 9.87 (br.s, 1H), 7.55 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.46 (d, 1H, <sup>3</sup>J = 8.3 Hz), 7.28 (t, 1H, <sup>3</sup>J = 7.6 Hz), 7.09 (ddd, 1H, <sup>3</sup>J = 8.0 Hz, <sup>3</sup>J = 7.1 Hz, <sup>4</sup>J = 0.9 Hz), 6.95 (d, 2H, <sup>3</sup>J = 8.4 Hz), 6.54 (d, 2H, <sup>3</sup>J = 8.5 Hz), 4.11 (s, 2H), 3.98 (br.s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 146.9, 136.8, 130.0, 129.7, 127.9, 125.4, 123.4 (q, <sup>1</sup>J<sub>CF</sub> = 268.1 Hz), 122.1 (q, <sup>2</sup>J<sub>CF</sub> = 36.6 Hz), 121.4, 121.0, 115.4, 112.9, 29.2. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -56.8 (s, 3F). HRMS (ESI-TOF): m/z [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>N<sub>2</sub><sup>+</sup>: 291.1104; found: 291.1110.

**3-((2-(Trifluoromethyl)-1H-indol-3-yl)methyl)aniline (4k).** Obtained using conditions C (0.120 g,



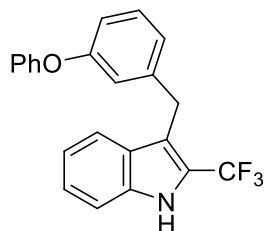
0.328 mmol of **3k**). Pale yellow solid, m.p. 138-140 °C, yield 0.086 g (90%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.56 (br.s, 1H), 7.56 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.26-7.35 (m, 2H), 7.05-7.15 (m, 2H), 6.72 (d, 2H, <sup>3</sup>J = 7.6 Hz), 6.57 (br.s, 1H), 6.53 (dd, 1H, <sup>3</sup>J = 7.9 Hz, <sup>3</sup>J = 1.7 Hz), 4.20 (s, 2H), 3.54 (br.s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 146.2, 141.3, 135.3, 129.2, 127.5, 124.7, 121.97 (q, <sup>2</sup>J<sub>CF</sub> = 36.5 Hz), 122.02 (q, <sup>1</sup>J<sub>CF</sub> = 268.7 Hz), 120.8, 120.5, 118.9, 116.6 (q, <sup>3</sup>J<sub>CF</sub> = 2.4 Hz), 115.2, 113.2, 111.6, 29.65. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -58.9 (s, 3F). HRMS (ESI-TOF): m/z [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>N<sub>2</sub><sup>+</sup>: 291.1104; found: 291.1111.

**2-((2-(Trifluoromethyl)-1H-indol-3-yl)methyl)aniline (4l).** Obtained using conditions C (0.160 g,



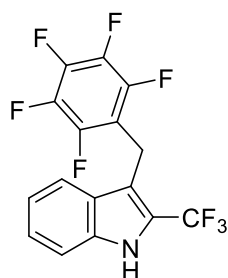
0.437 mmol of **3l**). Purified by column chromatography, using gradient elution by CH<sub>2</sub>Cl<sub>2</sub> followed by mixture CH<sub>2</sub>Cl<sub>2</sub>-MeOH (100:1, 30:1). Pale yellow solid, m.p. 136-138 °C, yield 0.097 g (76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.50 (br.s, 1H), 7.40 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.35 (d, 1H, <sup>3</sup>J = 8.2 Hz), 7.29 (t, 1H, <sup>3</sup>J = 7.5 Hz), 7.08-7.12 (m, 1H), 7.04-7.08 (m, 1H), 6.93 (d, 1H, <sup>3</sup>J = 7.5 Hz), 6.67-6.75 (m, 2H), 4.13 (s, 2H), 3.53 (br.s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 144.2, 135.3, 129.5, 127.5, 127.4, 124.9, 123.9, 122.4 (q, <sup>2</sup>J<sub>CF</sub> = 36.8 Hz), 121.9 (q, <sup>1</sup>J<sub>CF</sub> = 269.0 Hz), 120.9, 120.7, 118.8, 115.7, 115.0 (q, <sup>3</sup>J<sub>CF</sub> = 2.9 Hz), 111.7, 25.9. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.3 (s, 3F). HRMS (ESI-TOF): m/z [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>14</sub>F<sub>3</sub>N<sub>2</sub><sup>+</sup>: 291.1104; found: 291.1104.

**3-(3-Phenoxybenzyl)-2-(trifluoromethyl)-1H-indole (4m).** Obtained using conditions B (0.126 g, 0.305 mmol of **3m**). Pale yellow solid, m.p. 71-73 °C, yield



0.107 g (96%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  8.33 (br.s, 1H), 7.56 (d, 1H,  $^3J = 8.1$  Hz), 7.31-7.41 (m, 4H), 7.22-7.27 (m, 1H), 7.10-7.20 (m, 2H), 6.97-7.07 (m, 4H), 6.86 (dd, 1H,  $^3J = 8.1$  Hz,  $^4J = 1.7$  Hz), 4.29 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  157.14, 157.11, 142.1, 135.3, 129.6, 127.3, 124.8, 123.3, 123.1, 122.1 (q,  $^2J_{\text{CF}} = 36.7$  Hz), 121.9 (q,  $^1J_{\text{CF}} = 269.0$  Hz), 120.69, 120.65, 119.1, 118.7, 116.5, 116.3 (q,  $^3J_{\text{CF}} = 2.5$  Hz), 111.7, 29.6.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -59.1 (s, 3F). HRMS (ESI-TOF):  $m/z$   $[\text{M-H}]^-$  Calcd for  $\text{C}_{22}\text{H}_{15}\text{F}_3\text{NO}^-$ : 366.1111; found: 366.1107.

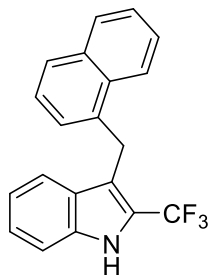
**3-((Perfluorophenyl)methyl)-2-(trifluoromethyl)-1H-indole (4n).** Obtained using conditions B



(0.117 g, 0.285 mmol of **3n**). Purified by column chromatography, using gradient elution by mixture hexane- $\text{CH}_2\text{Cl}_2$  (4:1) followed by mixture hexane- $\text{CH}_2\text{Cl}_2$  (2:1). Pale brown solid, m.p. 131-133 °C, yield 0.082 g (79%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  8.32 (br.s, 1H), 7.56 (d, 1H,  $^3J = 8.1$  Hz), 7.37-7.42 (m, 1H), 7.29-7.36 (m, 1H), 7.19 (ddd, 1H,  $^3J = 8.1$  Hz,  $^3J = 6.9$  Hz,  $^4J = 1.1$  Hz), 4.32 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  145.3 (dddt,  $^1J_{\text{CF}} = 246.8$  Hz,  $^3J_{\text{CF}} = 11.8$  Hz,  $^4J_{\text{CF}} = 7.8$  Hz,  $^5J_{\text{CF}} = 3.8$  Hz, CF), 140.04 (dm,  $^1J_{\text{CF}} = 258.6$  Hz,  $m_1$  141.5-141.1,  $m_2$  138.9-138.6, CF), 137.5 (dm,  $^1J_{\text{CF}} = 257.8$  Hz,  $m_1$  138.9-138.6,  $m_2$  136.5-136.1, CF), 135.0, 126.6, 125.1, 122.3 (q,  $^2J_{\text{CF}} = 37.4$  Hz), 121.7 (q,  $^1J_{\text{CF}} = 269.1$  Hz), 121.1, 119.7, 113.1, 112.9, 111.9, 29.8 (d,  $^3J_{\text{CF}} = 20.6$  Hz, CF).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -59.7 (s, 3F), -142.98 - -143.23 (m, 2F), -157.9 (t, 1F,  $J = 20.8$  Hz), -163.47 - -163.67 (m, 2F). HRMS (ESI-TOF):  $m/z$   $[\text{M-H}]^-$  Calcd for  $\text{C}_{16}\text{H}_6\text{F}_8\text{N}^-$ : 364.0378; found: 364.0373.

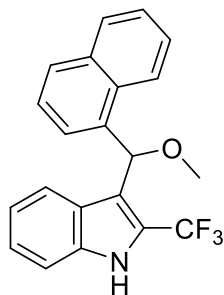
C16H7F8N

**3-(Naphthalen-1-ylmethyl)-2-(trifluoromethyl)-1H-indole (4o).** Obtained using conditions B



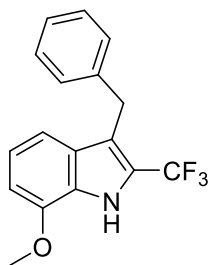
(0.043 g, 0.116 mmol of **3o**) and 8 equivalents of  $\text{NH}_4\text{HCO}_2$  (0.059 g, 0.94 mmol, 8 equiv.). White solid, m.p. 69-71 °C, yield 0.0328 g (87%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  8.37 (br.s, 1H), 8.29 (d, 1H,  $^3J = 8.4$  Hz), 7.90-7.98 (m, 1H), 7.76 (d, 1H,  $^3J = 8.2$  Hz), 7.59-7.66 (m, 1H), 7.53-7.59 (m, 1H), 7.43 (d, 1H,  $^3J = 8.3$  Hz), 7.29-7.39 (m, 3H), 7.08 (ddd, 1H,  $^3J = 8.0$  Hz,  $^3J = 7.1$  Hz,  $^4J = 0.9$  Hz), 7.04 (dd, 1H,  $^3J = 7.1$  Hz,  $^4J = 0.9$  Hz), 4.78 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  135.4, 135.3, 133.6, 131.9, 128.8, 127.7, 126.9, 126.1, 125.6, 125.5, 125.4, 124.9, 123.2, 122.7 (q,  $^2J_{\text{CF}} = 36.7$  Hz), 122.0 (q,  $^1J_{\text{CF}} = 269.3$  Hz), 120.9, 120.7, 115.7 (q,  $^3J_{\text{CF}} = 2.9$  Hz), 111.7, 26.6.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -59.7 (s, 3F). HRMS (ESI-TOF):  $m/z$   $[\text{M-H}]^-$  Calcd for  $\text{C}_{20}\text{H}_{13}\text{F}_3\text{N}^-$ : 324.1006; found: 324.1002.

**3-(Methoxy(naphthalen-1-yl)methyl)-2-(trifluoromethyl)-1H-indole (6b).**



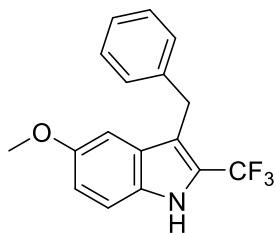
Obtained using conditions B (0.153 g, 0.412 mmol of **3o**) as a mixture with indole **4o** (yield 0.069 g (51%)) for **4o**). Purified by column chromatography, using mixture of hexane and CH<sub>2</sub>Cl<sub>2</sub> (1:1) as an eluent. Yellow powder, m.p. 65-67 °C, yield 0.041 g (28%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.53 (br.s, 1H), 8.17 (d, 1H, <sup>3</sup>J = 8.5 Hz), 7.88 (dd, 1H, <sup>3</sup>J = 8.3 Hz, <sup>4</sup>J = 0.9 Hz), 7.81 (d, 1H, <sup>3</sup>J = 8.0 Hz), 7.74 (d, 1H, <sup>3</sup>J = 8.2 Hz), 7.53-7.60 (m, 1H), 7.47-7.53 (m, 1H), 7.40 (d, 2H, <sup>3</sup>J = 8.2 Hz), 7.36 (d, 1H, <sup>3</sup>J = 7.9 Hz), 7.28-7.34 (m, 1H), 7.06-7.13 (m, 1H), 6.51 (s, 1H), 3.54 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 135.6, 135.3, 134.0, 131.6, 128.9, 128.7, 126.5, 126.3, 125.6, 125.3, 124.98, 124.94, 123.8, 123.3 (q, <sup>2</sup>J<sub>CF</sub> = 37.4 Hz), 123.0, 121.7 (q, <sup>1</sup>J<sub>CF</sub> = 269.5 Hz), 121.2, 116.5 (q, <sup>3</sup>J<sub>CF</sub> = 2.6 Hz), 111.7, 75.5, 57.2. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.0 (s, 3F). HRMS (ESI-TOF): m/z [M-OMe]<sup>-</sup> Calcd for C<sub>20</sub>H<sub>14</sub>F<sub>3</sub>N<sup>-</sup>: 324.1002; found: 324.1006.

**3-Benzyl-7-methoxy-2-(trifluoromethyl)-1H-indole (4p).** Obtained using conditions B (0.053 g,



0.151 mmol of **3p**). Green-yellowish viscous oil, yield 0.044 g (96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.57 (br.s, 1H), 7.23-7.30 (m, 4H), 7.15-7.22 (m, 1H), 7.11 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.04 (t, 1H, <sup>3</sup>J = 7.6 Hz), 6.72 (d, 1H, <sup>3</sup>J = 7.6 Hz), 4.26 (s, 2H), 3.97 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 146.3, 140.0, 128.7, 128.4, 128.3, 126.3, 126.0, 122.0 (q, <sup>1</sup>J<sub>CF</sub> = 268.9 Hz), 121.8 (q, <sup>2</sup>J<sub>CF</sub> = 36.8 Hz), 121.2, 117.1 (q, <sup>3</sup>J<sub>CF</sub> = 2.8 Hz), 113.1, 103.9, 55.4, 30.0. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.1 (s, 3F). HRMS (ESI-TOF): m/z [M-H]<sup>-</sup> Calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>-</sup>: 304.0955; found: 304.0960.

**3-Benzyl-5-methoxy-2-(trifluoromethyl)-1H-indole (4q).** Obtained using conditions B (0.098 g,



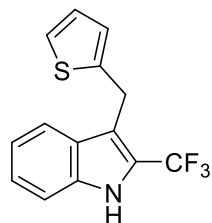
0.279 mmol of **3q**). Pale brown solid, m.p. 102-104 °C, yield 0.0826 g (97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.29 (br.s, 1H), 7.24-7.33 (m, 5H), 7.19-7.24 (m, 1H), 6.99 (dd, 1H, <sup>3</sup>J = 8.9 Hz, <sup>4</sup>J = 2.4 Hz), 6.92 (d, 1H, <sup>4</sup>J = 2.4 Hz), 4.27 (s, 2H), 3.78 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 154.5, 139.9, 130.5, 128.4, 128.3, 127.9, 126.1, 122.6 (q, <sup>2</sup>J<sub>CF</sub> = 36.7 Hz), 121.9 (q, <sup>1</sup>J<sub>CF</sub> = 269.0 Hz), 116.2 (q, <sup>3</sup>J<sub>CF</sub> = 2.4 Hz), 115.6, 112.6, 101.6, 55.7, 29.8. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.2 (s, 3F). HRMS (ESI-TOF): m/z [M-H]<sup>-</sup> Calcd for C<sub>17</sub>H<sub>13</sub>F<sub>3</sub>NO<sup>-</sup>: 304.0955; found: 304.0946.

**Reduction of ketone 3r.** Using conditions A: 12 mL vial with a screw cap was charged with ketone **3r** (0.072 g, 0.220 mmol), NH<sub>4</sub>HCO<sub>2</sub> (0.069 g, 1.10 mmol, 5 equiv.), Pd/C (10%, 0.012 g, 0.011 mmol, 5 mol%) and methanol (1.5 mL). Next, the reaction mixture was kept under stirring at 60 °C for 1 h. After that,

6M HCl (0.25 mL, 1.5 mmol) was added in 4-5 portions (evolution of CO<sub>2</sub>!). The reaction mixture was filtered through a short celite pad and dispersed between water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). Combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, volatiles were evaporated in vacuo, the residue was purified by column chromatography on silica gel, using gradient elution by mixture hexane-CH<sub>2</sub>Cl<sub>2</sub> (4:1) followed by mixture hexane-CH<sub>2</sub>Cl<sub>2</sub> (2:1) to give 3-(thiophen-2-ylmethyl)-2-(trifluoromethyl)-1H-indole (**4r**), yield 0.0048 g, (8%) and 3-(methoxy(thiophen-2-yl)methyl)-2-(trifluoromethyl)-1H-indole (**6c**), yield 0.035 g, (51%).

Using conditions D: 12 mL vial with a screw cap was charged with ketone **3r** (0.068 g, 0.208 mmol), NH<sub>4</sub>HCO<sub>2</sub> (0.188 g, 2.98 mmol, ~15 equiv.), Pd/C (10%, 0.011 g, 0.0104 mmol, 5 mol%) and methanol (3 mL). Next, the reaction mixture was kept under stirring for 1 day. After that, 6M HCl (0.5 mL, 3 mmol) was added in 4-5 portions (evolution of CO<sub>2</sub>!). The reaction mixture was filtered through a short celite pad and dispersed between water (10 mL) and CH<sub>2</sub>Cl<sub>2</sub> (20 mL). Aqueous layer was separated and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3×10 mL). Combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, volatiles were evaporated in vacuo, the residue was purified by column chromatography on silica gel, using gradient elution by mixture hexane-CH<sub>2</sub>Cl<sub>2</sub> (4:1) followed by mixture hexane-CH<sub>2</sub>Cl<sub>2</sub> (2:1) to give 3-(thiophen-2-ylmethyl)-2-(trifluoromethyl)-1H-indole (**4r**), yield 0.031 g, (53%) and 3-(methoxy(thiophen-2-yl)methyl)-2-(trifluoromethyl)-1H-indole (**6c**), yield 0.0038 g, (6%).

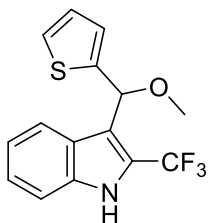
**3-(Thiophen-2-ylmethyl)-2-(trifluoromethyl)-1H-indole (4r).** White powder, m.p. 88-90 °C. <sup>1</sup>H



NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.26 (br.s, 1H), 7.63 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.37-7.42 (m, 1H), 7.29-7.35 (m, 1H), 7.17 (ddd, 1H, <sup>3</sup>J = 8.0 Hz, <sup>3</sup>J = 7.0 Hz, <sup>4</sup>J = 1.0 Hz), 7.10 (dd, 1H, <sup>3</sup>J = 5.1 Hz, <sup>4</sup>J = 1.2 Hz), 6.89 (dd, 1H, <sup>3</sup>J = 5.1 Hz, <sup>4</sup>J = 3.5 Hz), 6.80-6.86 (m, 1H), 4.44 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 143.0, 135.2, 127.0, 126.7, 125.0, 124.8, 123.6, 121.8 (q, <sup>1</sup>J<sub>CF</sub> = 269.0 Hz), 121.7 (q, <sup>2</sup>J<sub>CF</sub> = 36.8 Hz), 120.8, 120.5, 116.4 (q, <sup>3</sup>J<sub>CF</sub> = 2.7 Hz), 111.7, 24.2. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376.5 MHz): δ -59.3 (s, 3F). HRMS (ESI-TOF): m/z [M-H]<sup>+</sup>

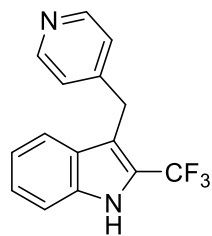
Calcd for C<sub>14</sub>H<sub>9</sub>F<sub>3</sub>NOS<sup>+</sup>: 280.0402; found: 280.0404.

**3-(Methoxy(thiophen-2-yl)methyl)-2-(trifluoromethyl)-1H-indole (6c).** Grey solid, m.p. 110-112



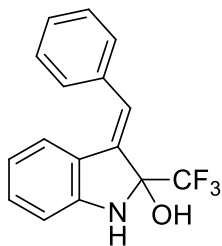
°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400.1 MHz): δ 8.43 (br.s, 1H), 7.90 (d, 1H, <sup>3</sup>J = 8.1 Hz), 7.39 (d, 1H, <sup>3</sup>J = 8.3 Hz), 7.32 (t, 1H, <sup>3</sup>J = 7.6 Hz), 7.23 (d, 1H, <sup>3</sup>J = 5.0 Hz), 7.15 (t, 1H, <sup>3</sup>J = 7.5 Hz), 6.86-6.92 (m, 1H), 6.83 (d, 1H, <sup>4</sup>J = 3.4 Hz), 6.03 (s, 1H), 3.41 (s, 3H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz): δ 145.1, 135.3, 126.4, 125.2, 125.1, 125.0, 124.7, 123.0, 122.9 (q, <sup>2</sup>J<sub>CF</sub> = 37.3 Hz), 121.6 (q, <sup>1</sup>J<sub>CF</sub> = 269.4 Hz), 121.1, 117.3 (q, <sup>3</sup>J<sub>CF</sub> = 2.6 Hz), 111.7, 74.3,

56.8.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -58.5 (s, 3F). HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{15}\text{H}_{12}\text{F}_3\text{NOS}^+$ : 334.0484; found: 334.0475.

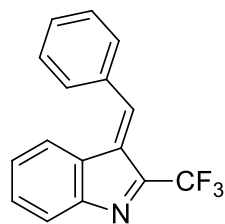


**Synthesis of 3-(pyridin-4-ylmethyl)-2-(trifluoromethyl)-1H-indole (4s).** 12 mL vial was charged with enamine **1a** (0.5 mmol), isonicotinaldehyde **2s** (0.0669 g, 0.625 mmol) and glacial acetic acid (1 mL). Reaction mixture was kept at 80-90  $^{\circ}\text{C}$  (hotplate stirrer) under stirring for 10 hours. The reaction mixture was cooled down to room temperature. Next, Pd/C (10%, 0.027 g, 0.025 mmol, 5 mol%) and formic acid (0.115 g, 2.5 mmol) was added and the reaction mixture was heated at 75  $^{\circ}\text{C}$  under stirring for 3 hours. The reaction mixture was filtered through a short celite pad and dispersed between water (10 mL) and  $\text{CH}_2\text{Cl}_2$  (20 mL). Aqueous layer was separated and extracted with  $\text{CH}_2\text{Cl}_2$  (3 $\times$ 10 mL). Combined organic phases were dried over  $\text{Na}_2\text{SO}_4$ , volatiles were evaporated in vacuo, the residue was purified by column chromatography on silica gel, using gradient elution by mixture hexane- $\text{CH}_2\text{Cl}_2$  (1:1) followed by  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{Cl}_2$ -MeOH (100:1) as eluents. Pale yellow-brown powder, m.p. 185-187  $^{\circ}\text{C}$ , yield 0.029 g (21%).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  9.03 (br.s, 1H), 8.42-8.50 (m, 2H), 7.46 (d, 1H,  $^3J = 8.1$  Hz), 7.43 (d, 2H,  $^3J = 8.3$  Hz), 7.32 (t, 1H,  $^3J = 7.6$  Hz), 7.11-7.18 (m, 3H), 4.26 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  150.5, 136.8, 127.8, 125.7, 124.4, 123.2 (q,  $^1J_{\text{CF}} = 268.2$  Hz), 123.1 (q,  $^2J_{\text{CF}} = 36.5$  Hz), 121.5, 121.0, 115.1 (q,  $^3J_{\text{CF}} = 2.7$  Hz), 113.1, 29.5.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -59.3 (s, 3F). HRMS (ESI-TOF):  $m/z$   $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{12}\text{F}_3\text{N}_2^+$ : 277.0947; found: 277.0950.

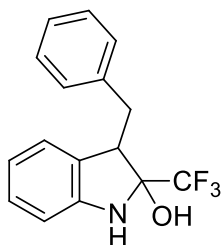
## NMR data of the reaction intermediates



**(E)-3-Benzylidene-2-(trifluoromethyl)indolin-2-ol (B).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  7.34-7.48 (m, 5H), 7.22 (d, 1H,  $^3J = 7.7$  Hz), 7.06-7.16 (m, 2H), 6.64-6.70 (m, 1H), 6.57-6.64 (m, 1H), 4.95 (s, 1H), 3.15 (br.s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  148.7, 137.0, 135.7, 130.6, 128.6, 128.4, 128.1, 127.8 (d,  $^4J_{\text{CF}} = 1.3$  Hz), 123.8, 123.3 (q,  $^1J_{\text{CF}} = 285.7$  Hz), 122.7, 119.6, 109.7, 90.4 (q,  $^2J_{\text{CF}} = 31.9$  Hz).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -85.4 (s, 3F).

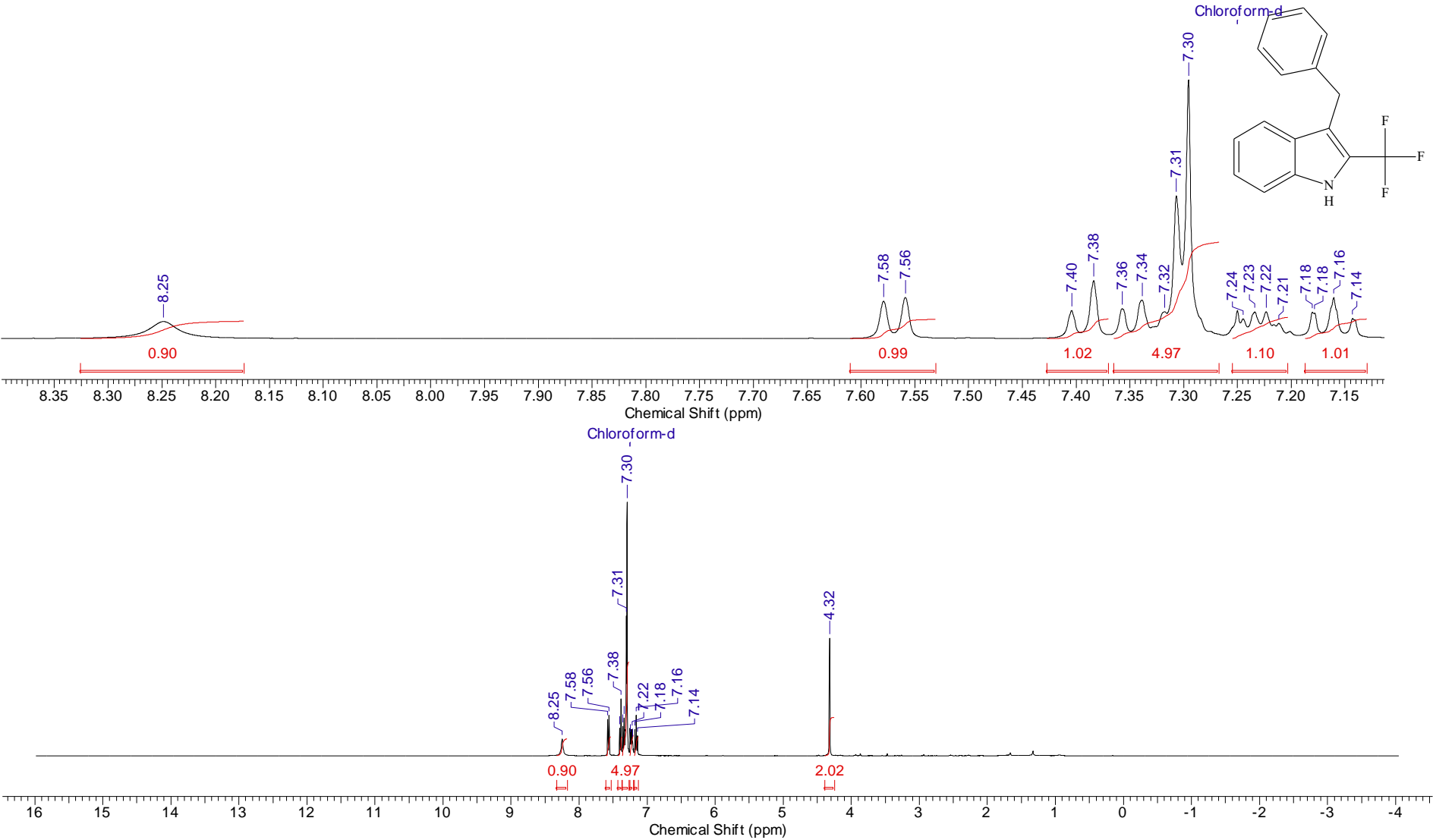


**(E)-3-Benzylidene-2-(trifluoromethyl)-3H-indole (C).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  7.95 (s, 1H), 7.67-7.78 (m, 3H), 7.50-7.56 (m, 3H), 7.40 (td, 1H,  $^3J = 7.6$  Hz,  $^4J = 1.1$  Hz), 7.15-7.28 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  158.2 (q,  $^2J_{\text{CF}} = 34.9$  Hz), 153.3, 142.7 (q,  $^4J_{\text{CF}} = 1.7$  Hz), 133.9, 133.0, 130.9, 130.0, 129.9, 128.9, 127.7, 122.9, 122.7, 120.7 (q,  $^1J_{\text{CF}} = 273.6$  Hz). For major isomer:  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -62.7 (s, 3F). For minor isomer:  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -61.7 (s, 3F).



**3-Benzyl-2-(trifluoromethyl)indolin-2-ol (D).**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400.1 MHz):  $\delta$  7.28-7.39 (m, 5H), 7.05-7.13 (m, 1H), 6.64-6.76 (m, 3H), 4.62 (s, 1H), 3.94 (dd, 1H,  $^3J = 9.6$  Hz,  $^3J = 5.2$  Hz), 3.37 (dd, 1H,  $^3J = 14.2$  Hz,  $^3J = 5.2$  Hz), 2.95 (dd, 1H,  $^3J = 14.2$  Hz,  $^3J = 9.7$  Hz), 2.79 (br.s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , 100.6 MHz):  $\delta$  145.6, 138.8, 129.1, 128.7, 128.6, 128.3, 126.7, 124.8, 124.0 (q,  $^1J_{\text{CF}} = 284.1$  Hz), 120.0, 92.5 (q,  $^2J_{\text{CF}} = 30.9$  Hz), 47.1, 34.4.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376.5 MHz):  $\delta$  -84.3 (s, 3F).

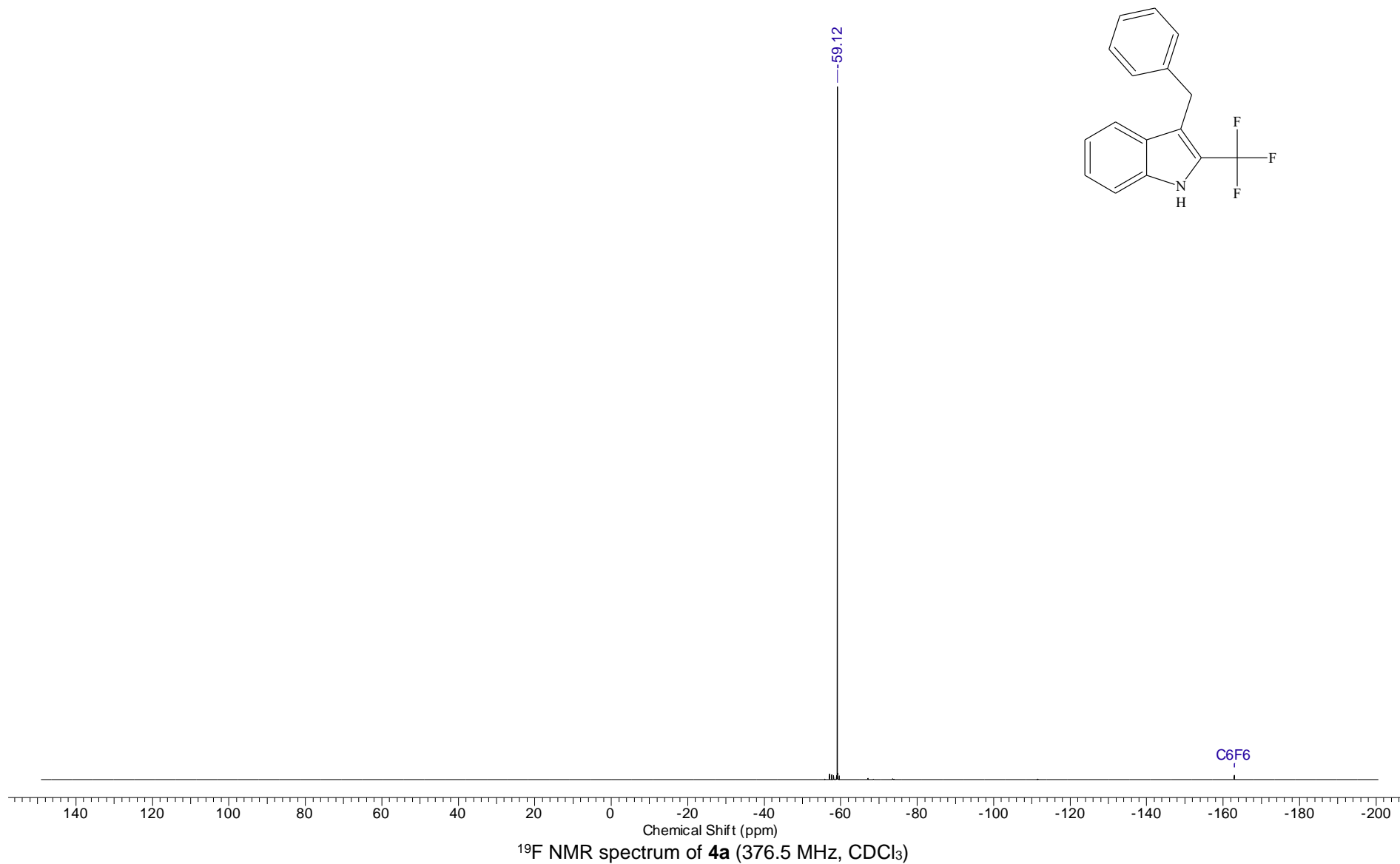
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| Nucleus                | <sup>1</sup> H                                    | Number of Transients | 4                    | Original Points Count | 32768                |
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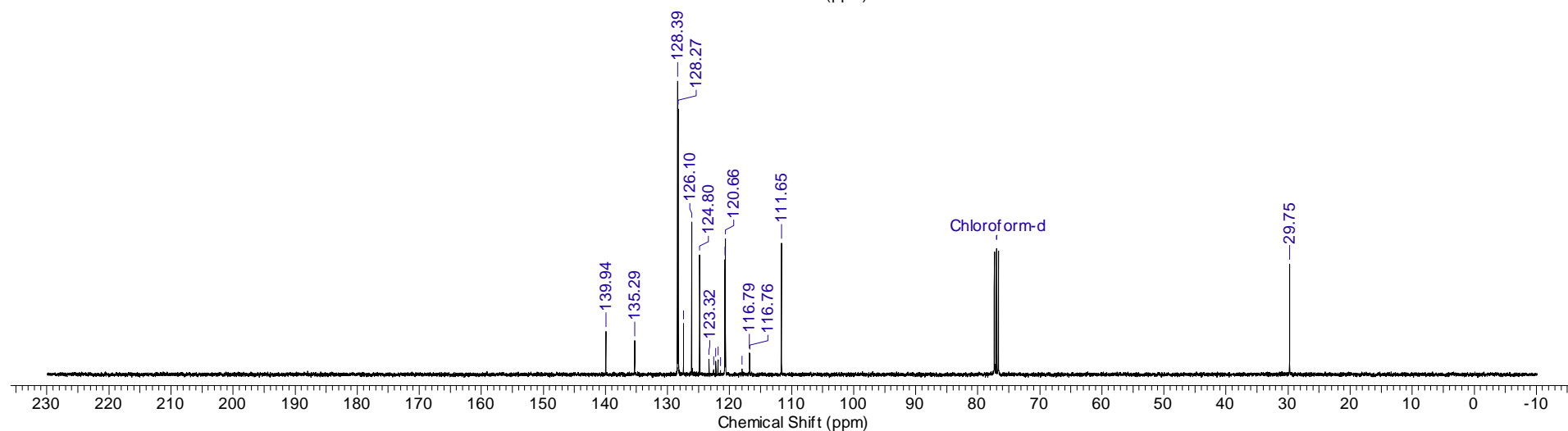
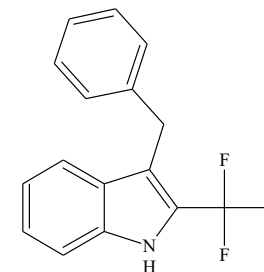
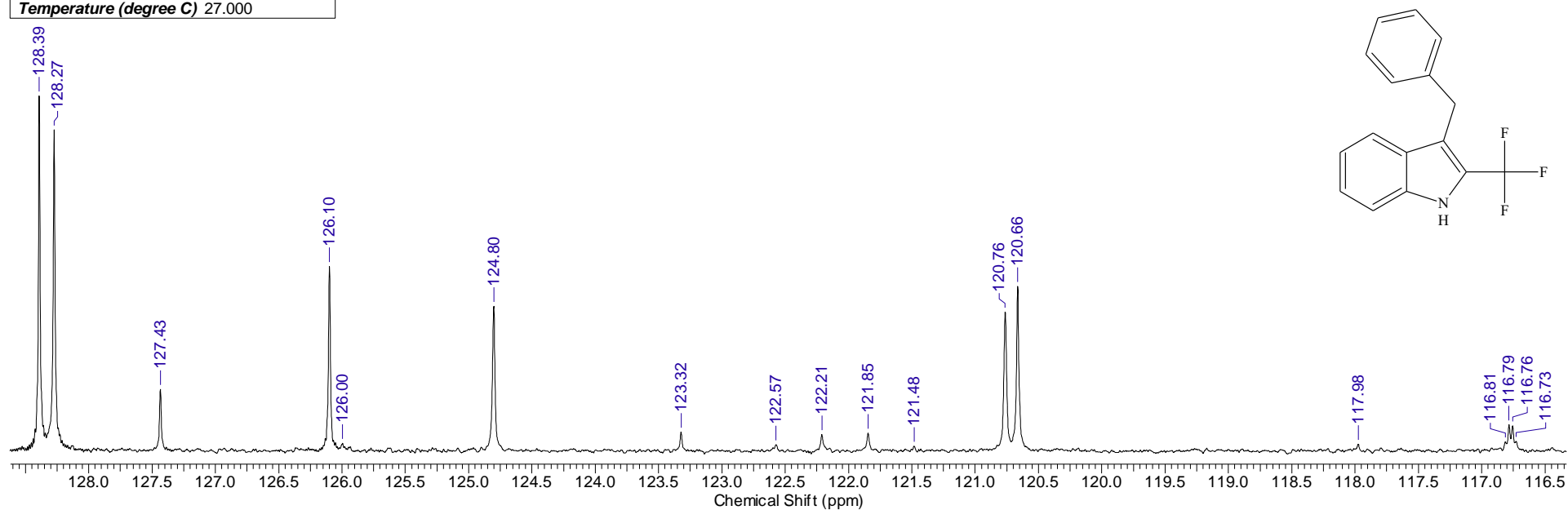


<sup>1</sup>H NMR spectrum of **4a** (400.1 MHz, CDCl<sub>3</sub>)

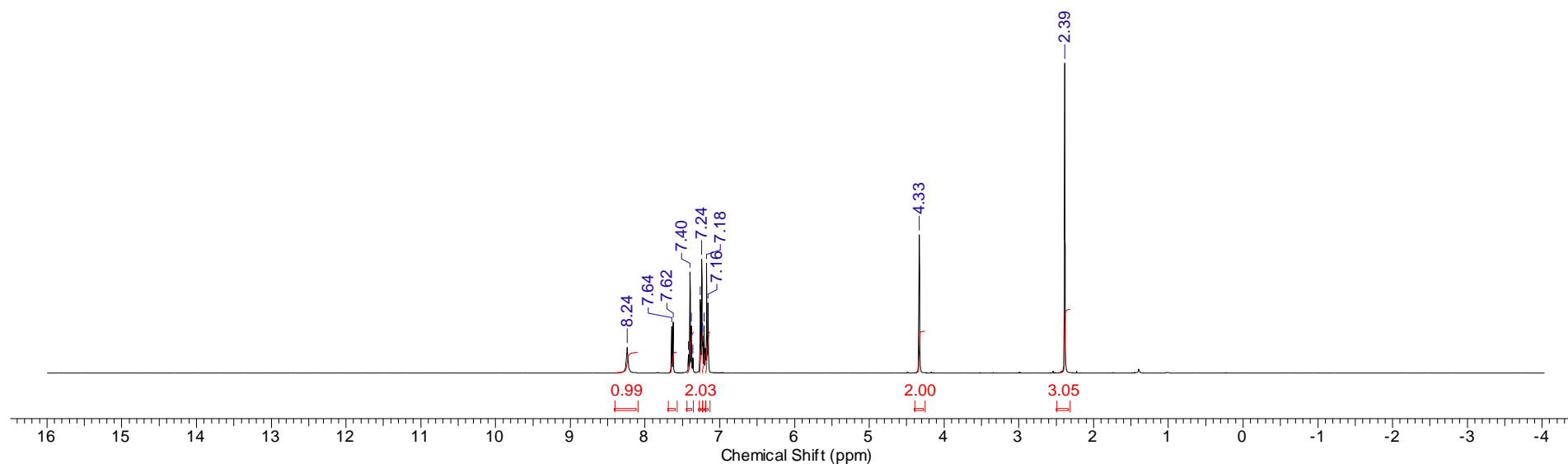
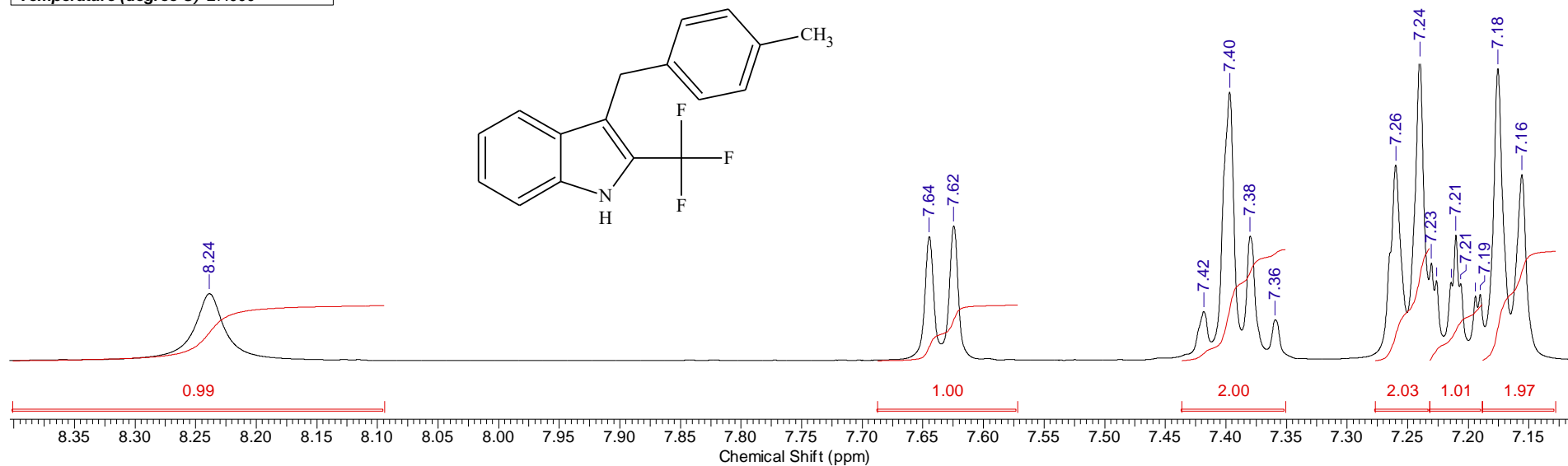


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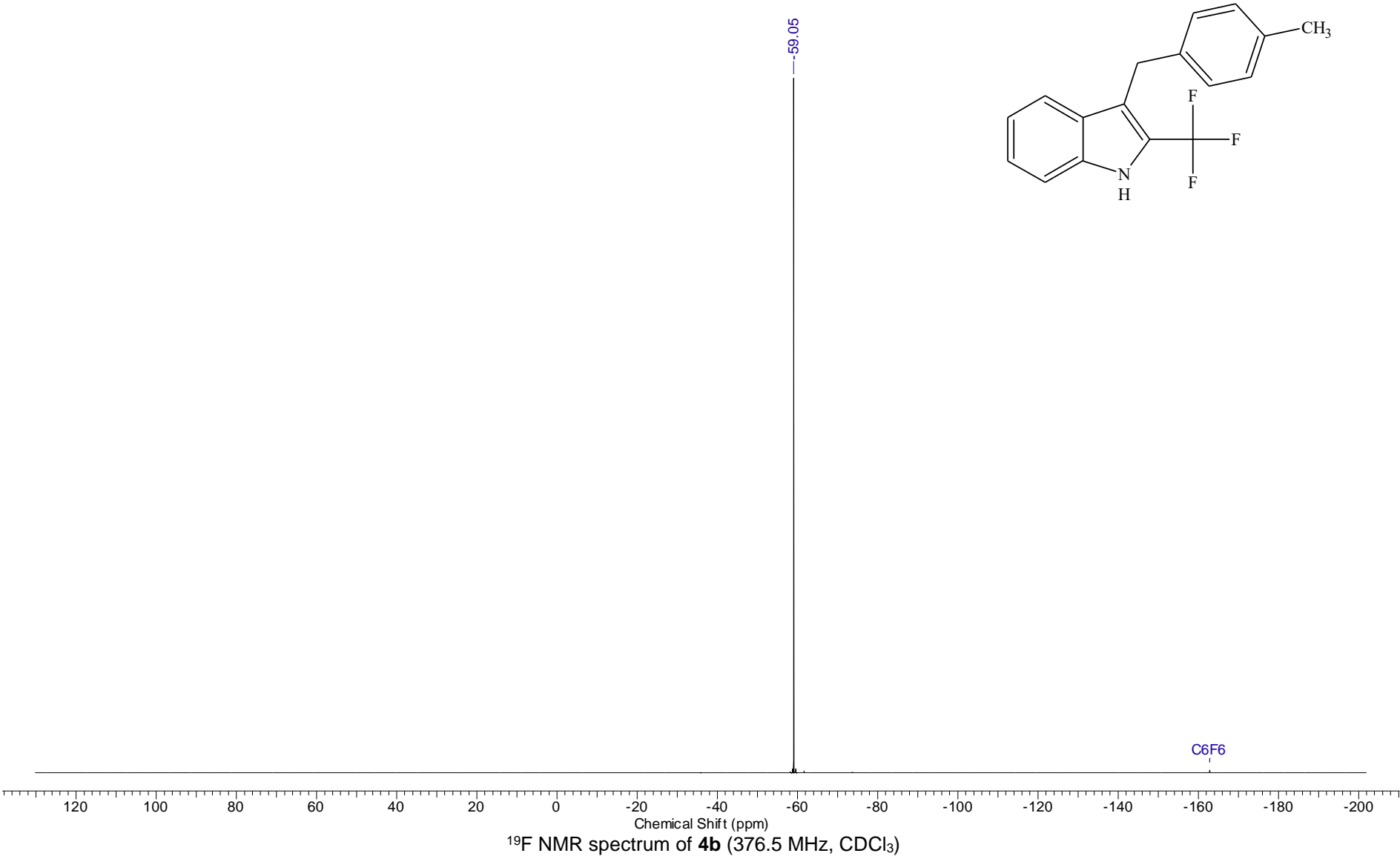


 $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4a** (100.6 MHz,  $\text{CDCl}_3$ )

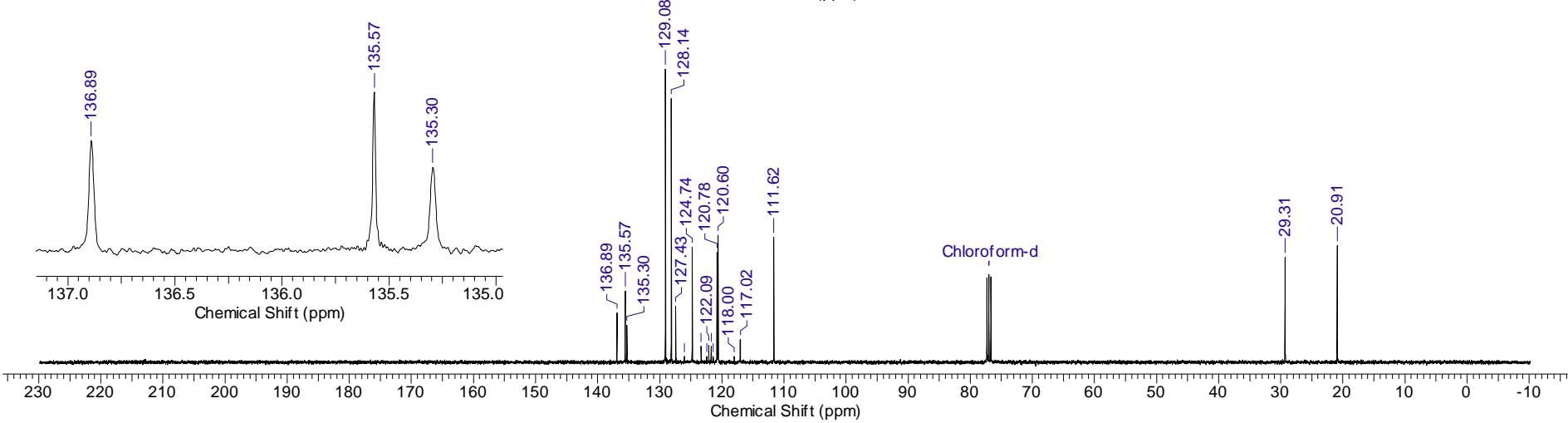
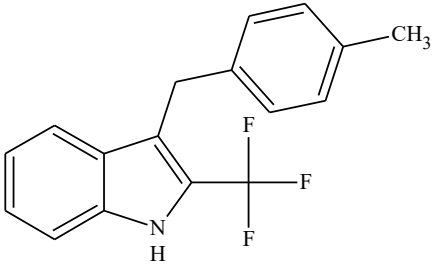
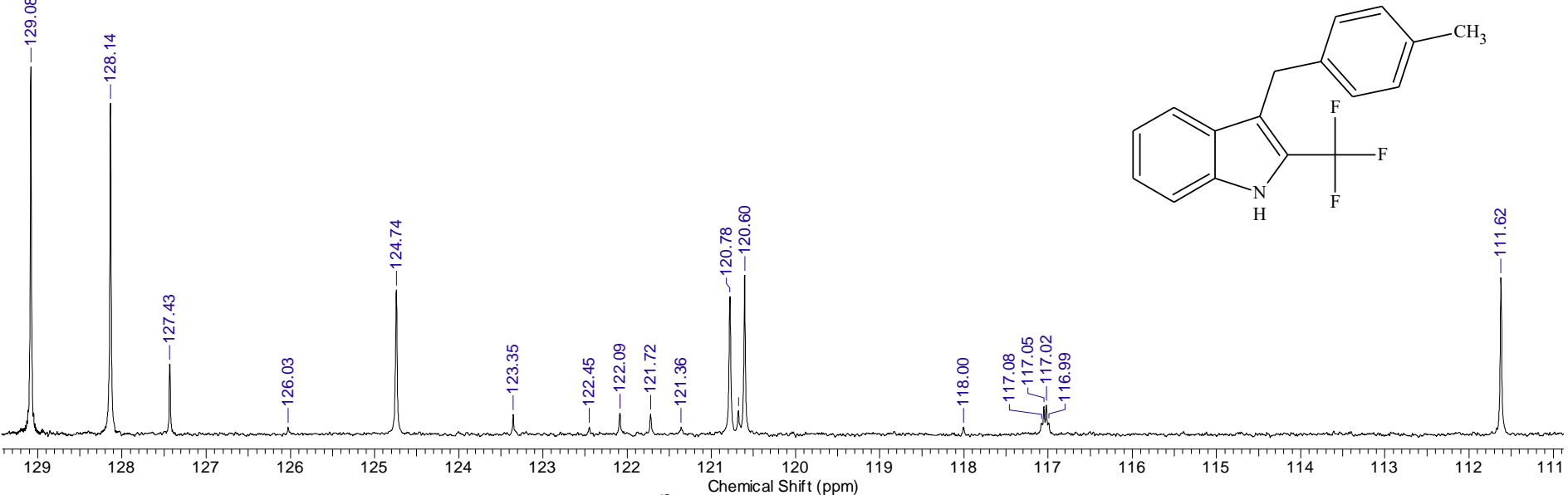
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|------------------------|--|----------------------|----------------------|-----------------------|-------|------------------|----------------------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UxNMR. |                       |       | Date             | 30 Oct 2019 17:51:48 |
| File Name              | C:\DOCS\OUTPUT_301\2019\10. 锐? 狙黑BM-1778.H_001001r |                      |                      |                       |       | Frequency (MHz)  | 400.13               |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768 | Points Count     | 131072               |
| Pulse Sequence         | zg30   | Solvent              | CHLOROFORM-D         |                       |       | Sweep Width (Hz) | 8012.82              |
| Temperature (degree C) | 27.000   |                      |                      |                       |       |                  |                      |

<sup>1</sup>H NMR spectrum of **4b** (400.1 MHz, CDCl<sub>3</sub>)

|                        |           |                        |             |                      |   |                              |
|------------------------|-----------|------------------------|-------------|----------------------|---|------------------------------|
| Acquisition Time (sec) | 1.5729    | Date                   | Oct 31 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.10.31\BM-1778-F_20191031_01\FLUORINE_01 |                              |
| Frequency (MHz)        | 376.33    | Nucleus                | 19F         | Number of Transients | 8   | Original Points Count 196608 |
| Points Count           | 262144    | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D  |                              |
| Sweep Width (Hz)       | 125000.00 | Temperature (degree C) | 30.000      |                      |   |                              |

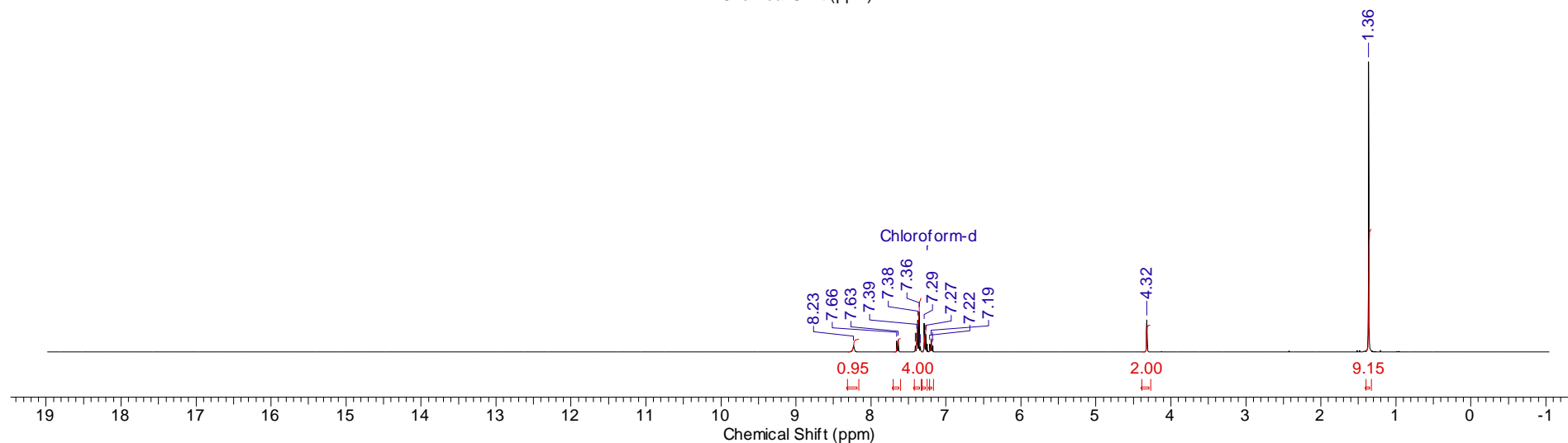
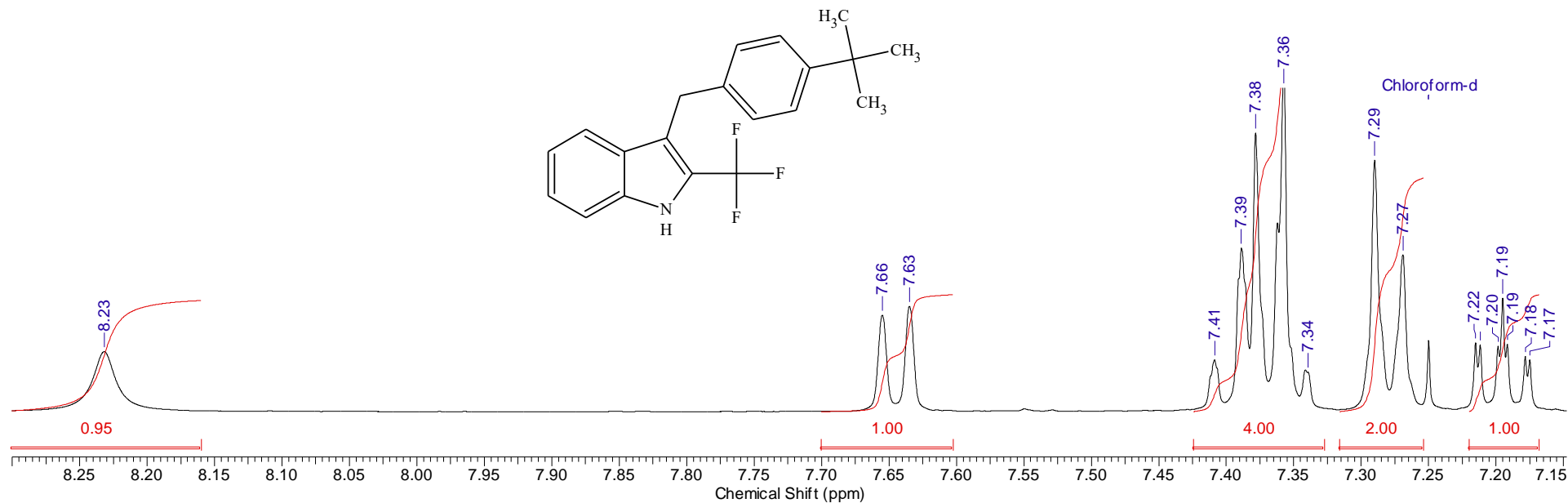


|                               |   |                             |                      |                              |                      |
|-------------------------------|---|-----------------------------|----------------------|------------------------------|----------------------|
| <b>Acquisition Time (sec)</b> | 0.6783                                      | <b>Comment</b>              | Imported from Uxnmr. | <b>Date</b>                  | 30 Oct 2019 17:57:40 |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\201910\BM-1778.C_002001r |                             |                      | <b>Frequency (MHz)</b>       | 100.61               |
| <b>Nucleus</b>                | <sup>13</sup> C                             | <b>Number of Transients</b> | 137                  | <b>Original Points Count</b> | 16384                |
| <b>Pulse Sequence</b>         | zgpg30                                      | <b>Solvent</b>              | CHLOROFORM-D         | <b>Points Count</b>          | 131072               |
| <b>Temperature (degree C)</b> | 27.000                                      |                             |                      | <b>Sweep Width (Hz)</b>      | 24154.59             |



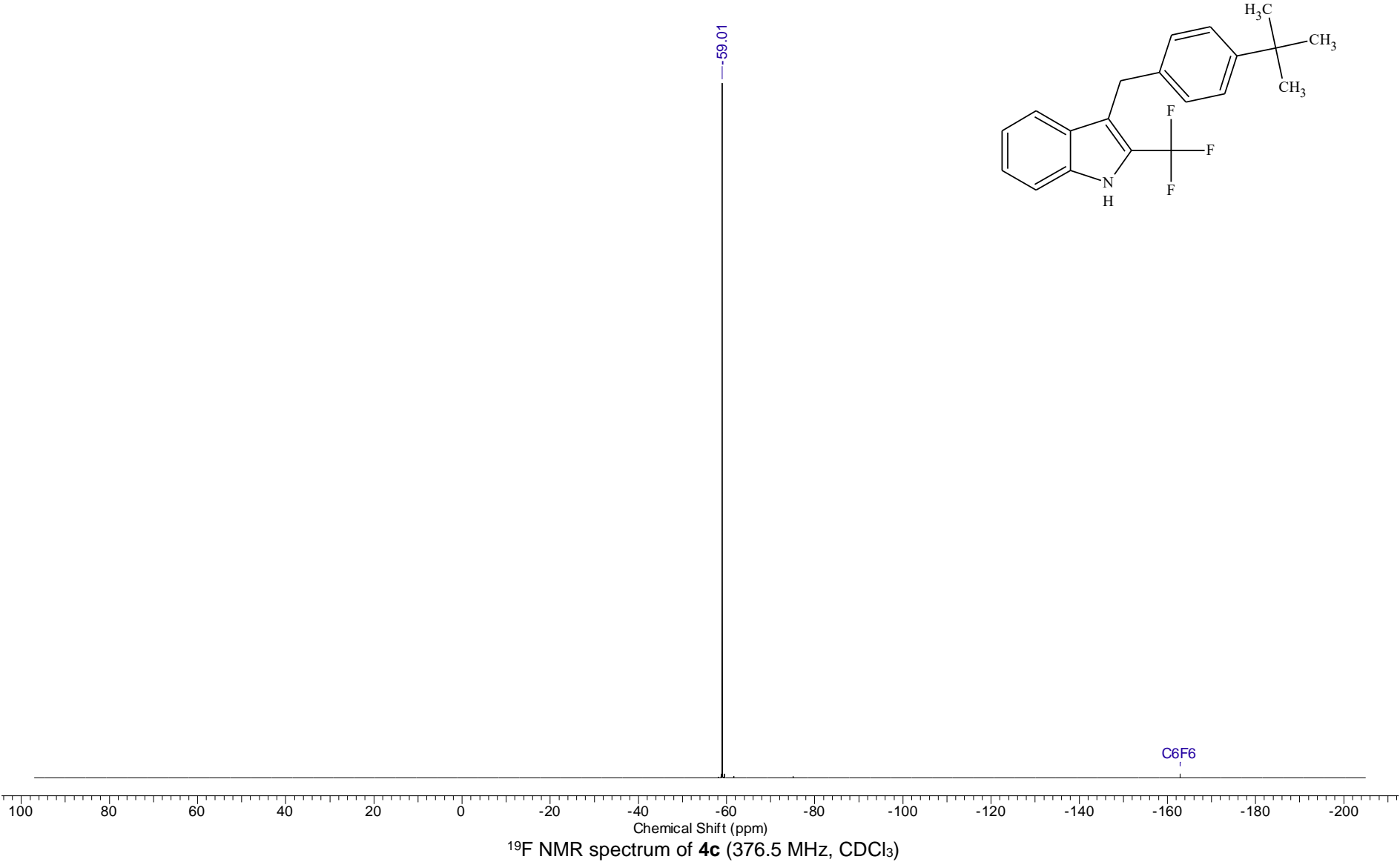
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4b** (100.6 MHz, CDCl<sub>3</sub>)

|                        |  |                      |                      |                       |                 |                        |        |
|------------------------|--|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UXMNR. |                       | Date            | 27 Nov 2019 17:46:56   |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙黒BM-1801.H_001001r |                      |                      |                       | Frequency (MHz) | 400.13                 |        |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768           | Points Count           | 131072 |
| Pulse Sequence         | zg30   | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 8012.82         | Temperature (degree C) | 27.000 |

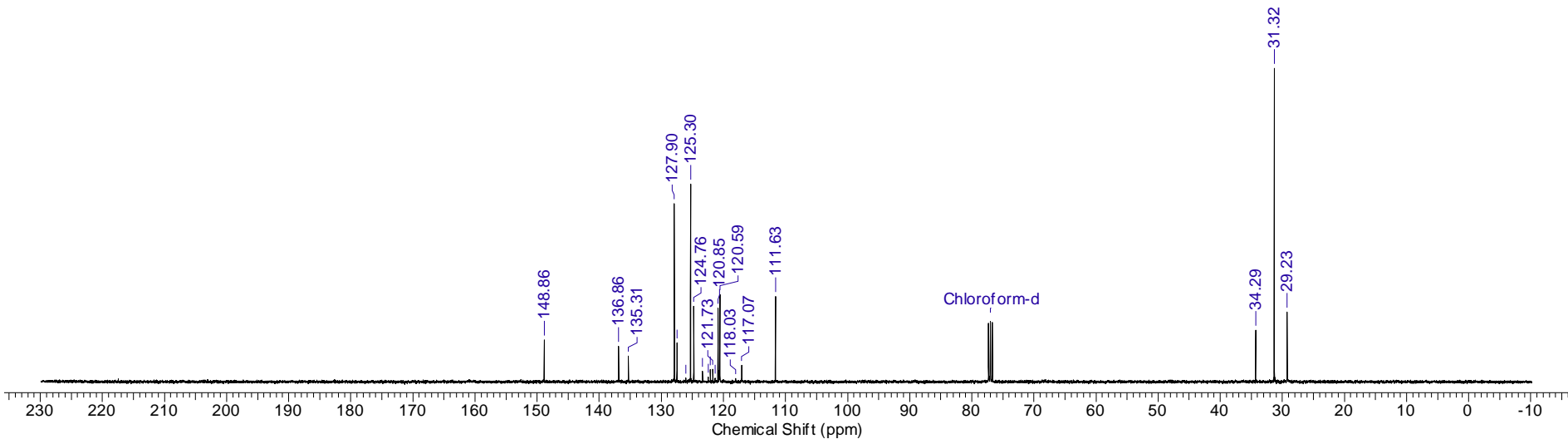
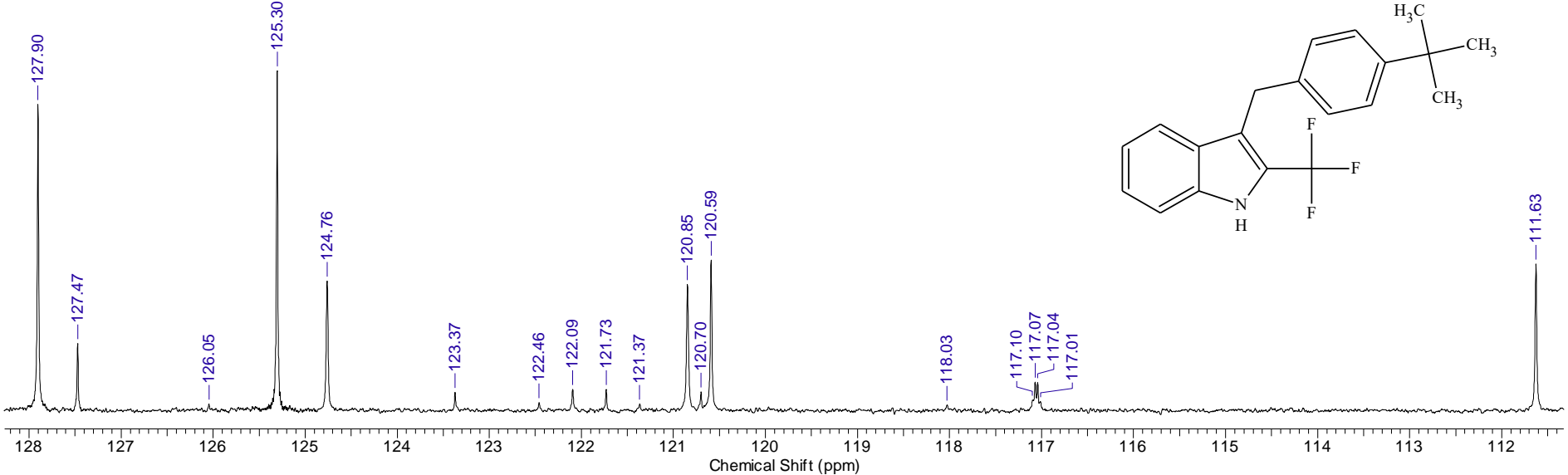


<sup>1</sup>H NMR spectrum of **4c** (400.1 MHz, CDCl<sub>3</sub>)

|                        |           |                        |             |                      |   |                              |
|------------------------|-----------|------------------------|-------------|----------------------|---|------------------------------|
| Acquisition Time (sec) | 2.3069    | Date                   | Nov 28 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.11.28\BM-1801-F_20191128_01\FLUORINE_01 |                              |
| Frequency (MHz)        | 376.32    | Nucleus                | 19F         | Number of Transients | 8   | Original Points Count 262144 |
| Points Count           | 262144    | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D  |                              |
| Sweep Width (Hz)       | 113636.37 | Temperature (degree C) | 22.000      |                      |   |                              |



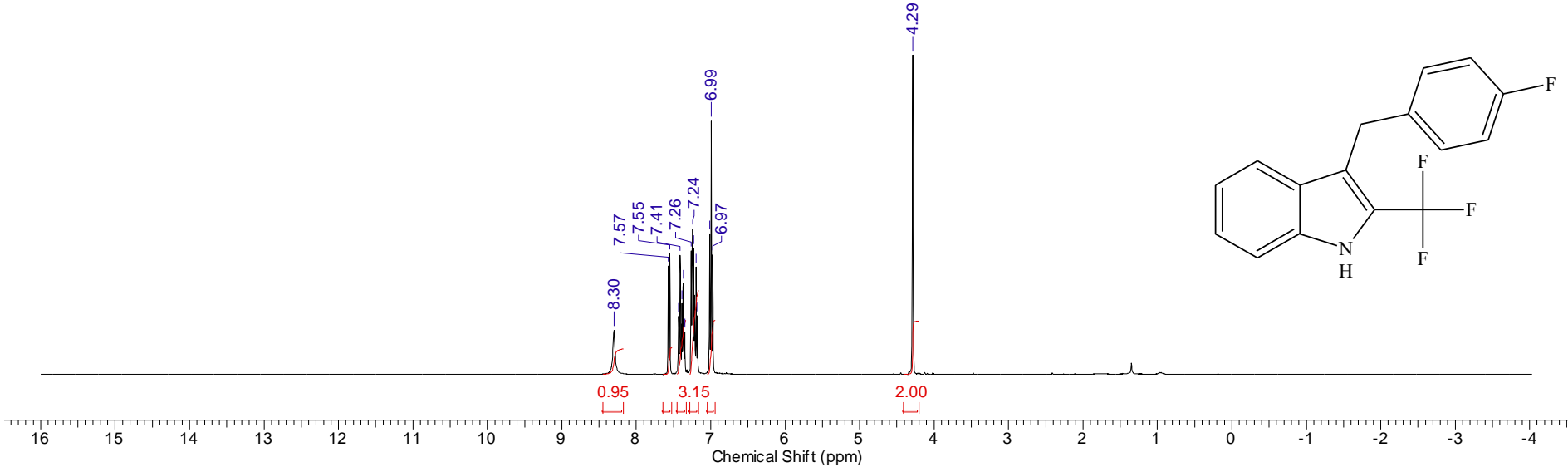
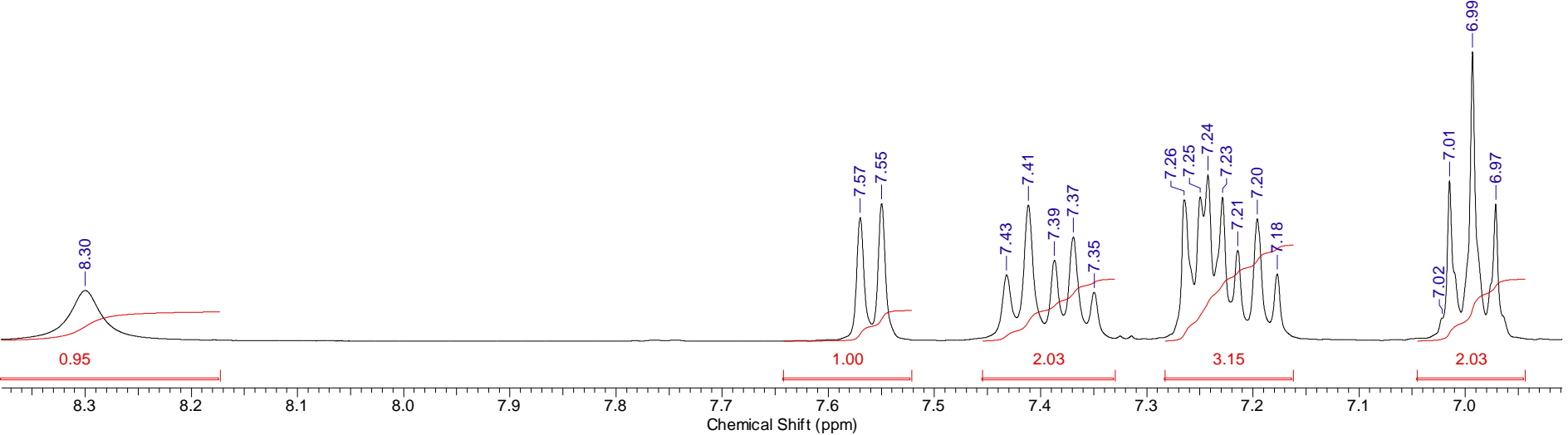
|                        |  |                       |                      |              |                        |                      |        |
|------------------------|--|-----------------------|----------------------|--------------|------------------------|----------------------|--------|
| Acquisition Time (sec) | 0.6783   | Comment               | Imported from UXNMR. |              | Date                   | 27 Nov 2019 17:50:18 |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙黒BM-1801.C_002001r |                       | Frequency (MHz)      | 100.61       | Nucleus                | 13C                  |        |
| Number of Transients   | 73   | Original Points Count | 16384                | Points Count | 131072                 | Pulse Sequence       | zgpg30 |
| Solvent                | CHLOROFORM-D                                     |                       | Sweep Width (Hz)     | 24154.59     | Temperature (degree C) | 27.000               |        |



<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4c** (100.6 MHz, CDCl<sub>3</sub>)

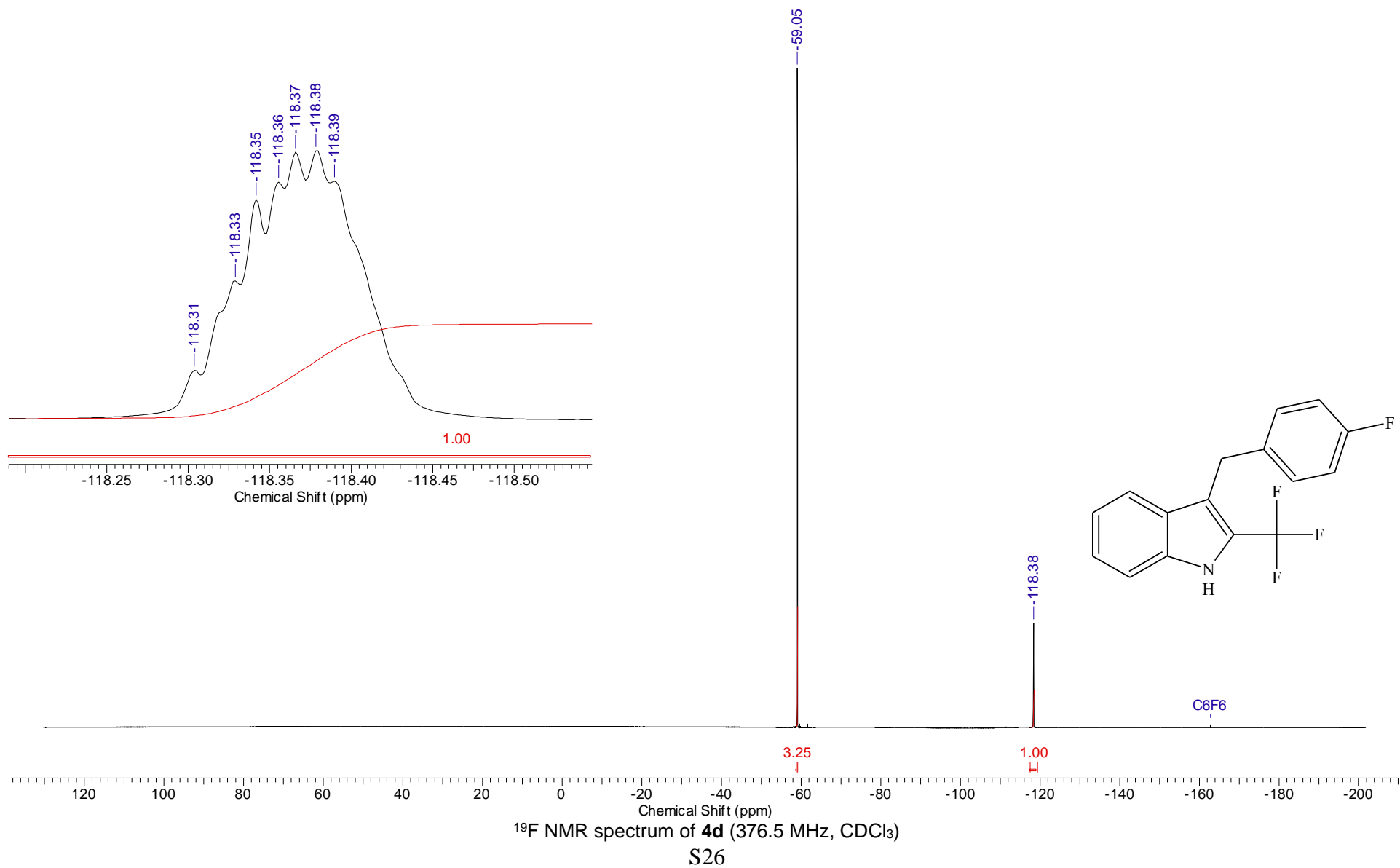


|                        |  |                              |         |                       |         |                        |                      |
|------------------------|--|------------------------------|---------|-----------------------|---------|------------------------|----------------------|
| Acquisition Time (sec) | 4.0894   | Comment Imported from UXNMR. |         |                       |         | Date                   | 01 Nov 2019 15:37:42 |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙黒BM-1780.H_001001r |                              |         |                       |         | Frequency (MHz)        | 400.13               |
| Nucleus                | 1H   | Number of Transients         | 4       | Original Points Count | 32768   | Points Count           | 131072               |
| Pulse Sequence         | zg30   | Solvent                      | DMSO-D6 | Sweep Width (Hz)      | 8012.82 | Temperature (degree C) | 27.000               |

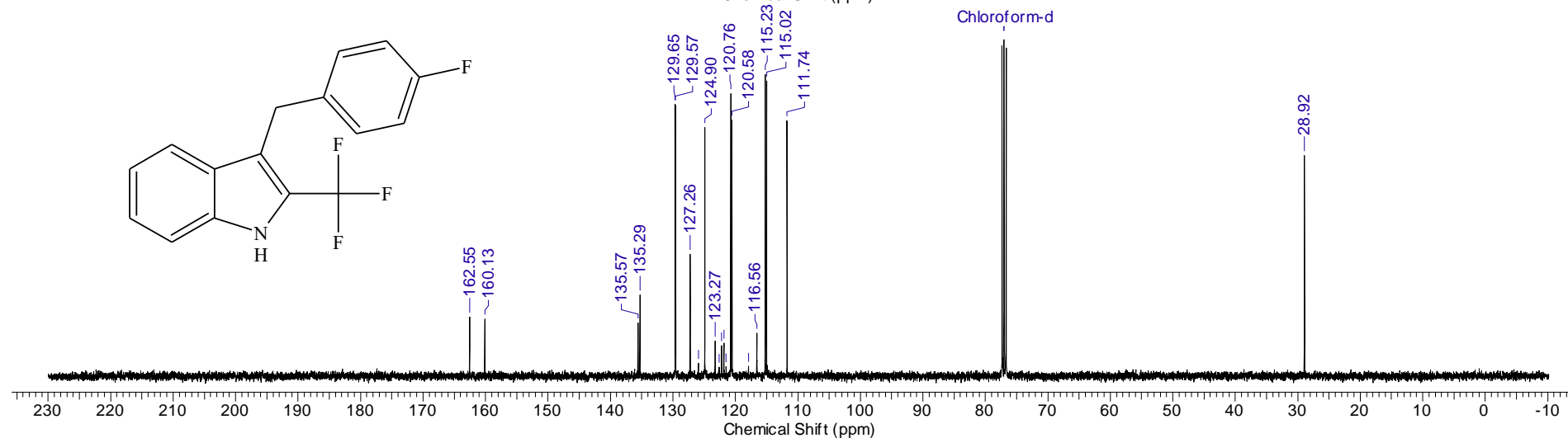
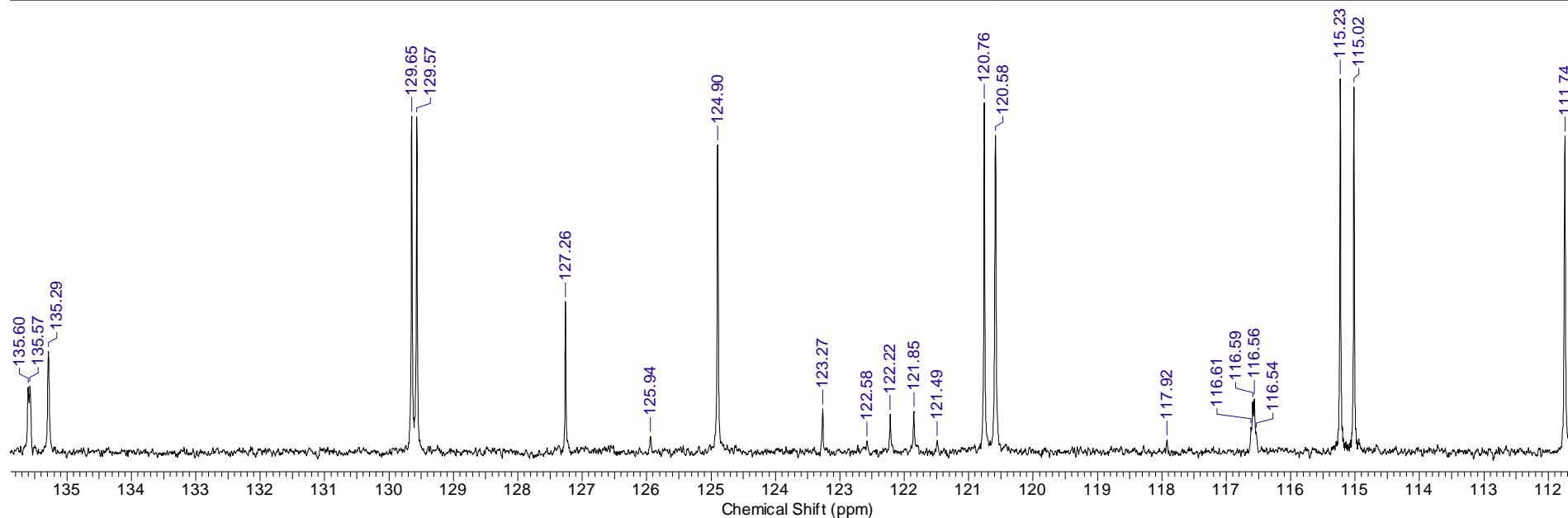


1H NMR spectrum of **4d** (400.1 MHz, CDCl<sub>3</sub>)

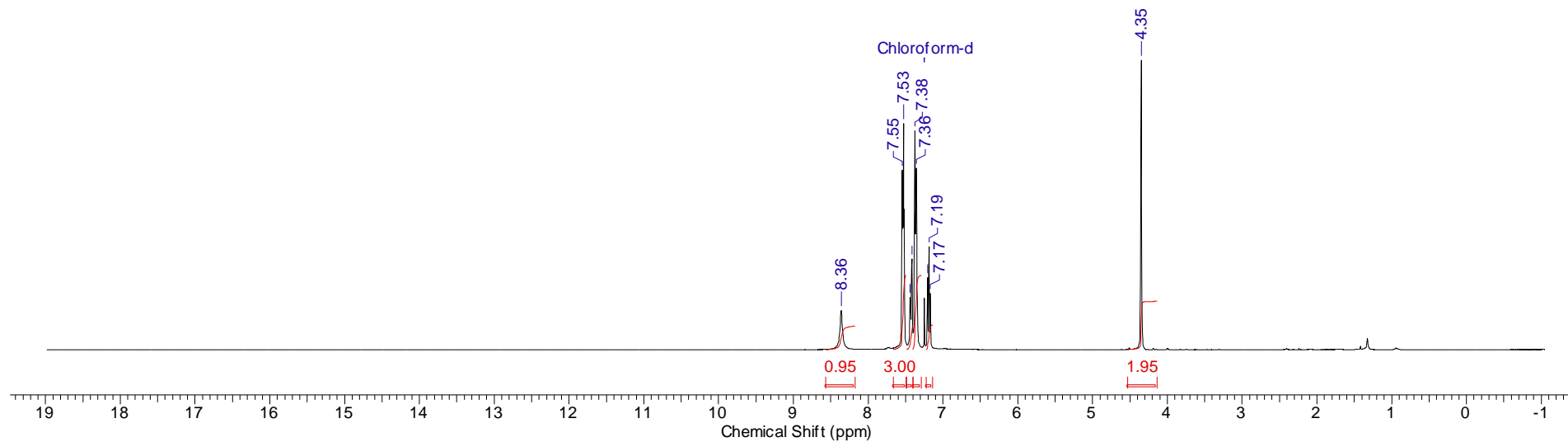
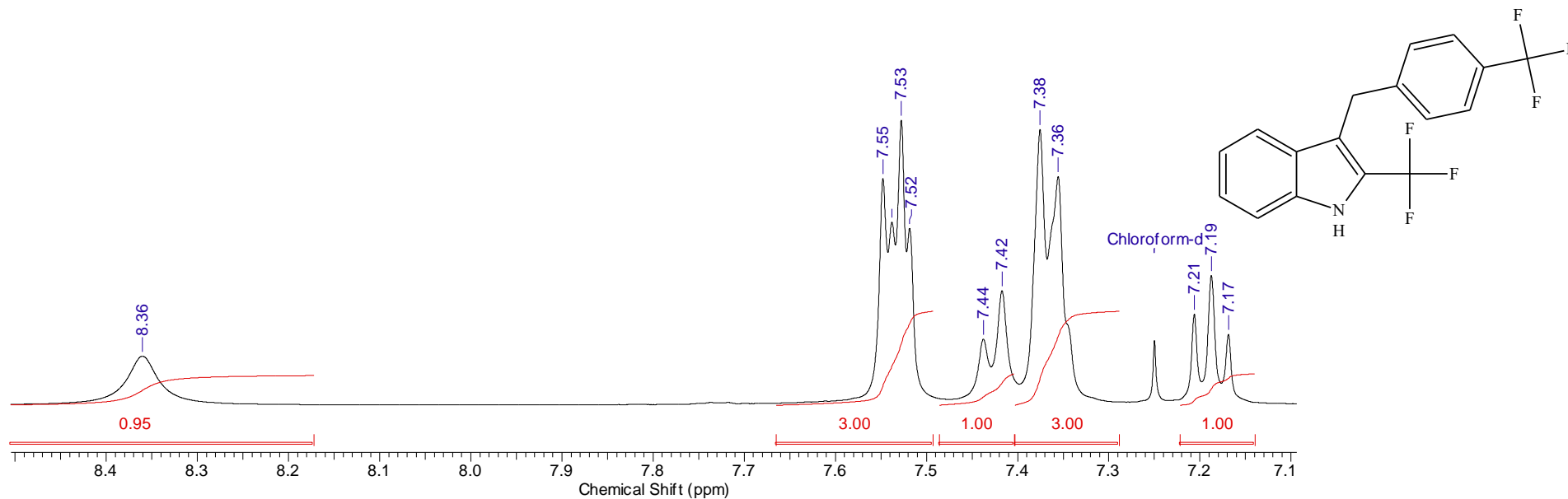
|                        |           |                        |            |                      |   |                              |
|------------------------|-----------|------------------------|------------|----------------------|---|------------------------------|
| Acquisition Time (sec) | 1.5729    | Date                   | Nov 7 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.11.07\BM-1780-F_20191107_01\FLUORINE_01 |                              |
| Frequency (MHz)        | 376.33    | Nucleus                | 19F        | Number of Transients | 8   | Original Points Count 196608 |
| Points Count           | 262144    | Pulse Sequence         | s2pul      | Solvent              | CHLOROFORM-D  |                              |
| Sweep Width (Hz)       | 125000.00 | Temperature (degree C) | 30.000     |                      |   |                              |



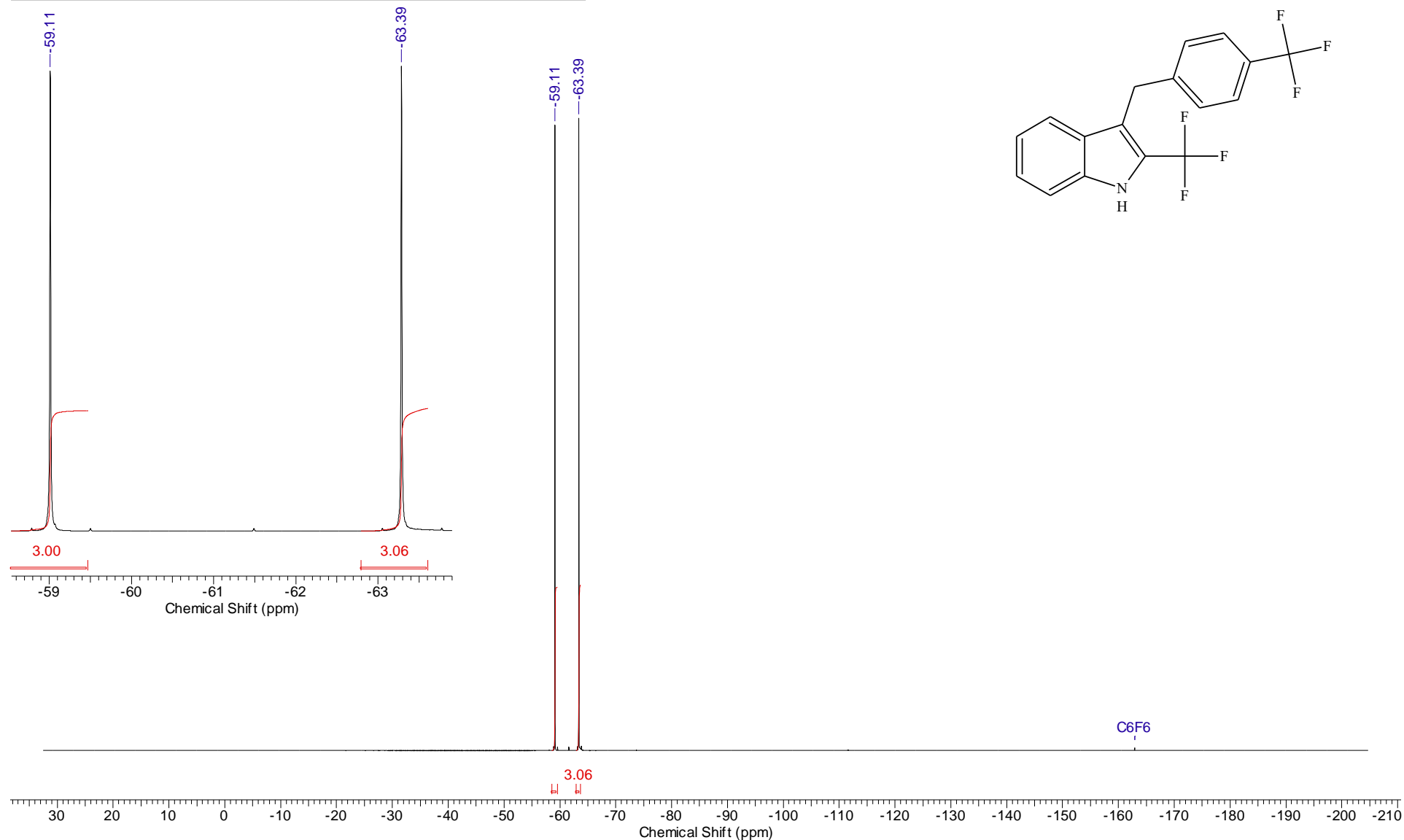
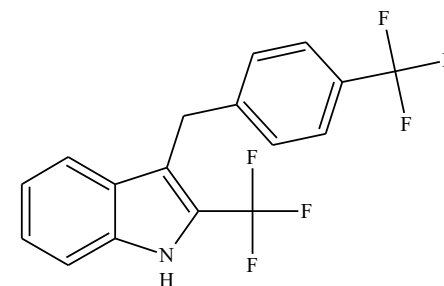
|                        |  |                       |                      |              |                        |                      |        |
|------------------------|--|-----------------------|----------------------|--------------|------------------------|----------------------|--------|
| Acquisition Time (sec) | 0.6783   | Comment               | Imported from UXNMR. |              | Date                   | 01 Nov 2019 15:42:56 |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙兎BM-1780.C_002001r |                       | Frequency (MHz)      | 100.61       | Nucleus                | 13C                  |        |
| Number of Transients   | 122  | Original Points Count | 16384                | Points Count | 131072                 | Pulse Sequence       | zgpg30 |
| Solvent                | CHLOROFORM-D                                     |                       | Sweep Width (Hz)     | 24154.59     | Temperature (degree C) | 27.000               |        |

 $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4d** (100.6 MHz,  $\text{CDCl}_3$ ).

|                        |  |                      |                      |                       |                 |                        |        |
|------------------------|--|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UXMNR. |                       | Date            | 27 Nov 2019 17:28:52   |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙鼎BM-1803.H_001001r |                      |                      |                       | Frequency (MHz) | 400.13                 |        |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768           | Points Count           | 131072 |
| Pulse Sequence         | zg30   | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 8012.82         | Temperature (degree C) | 27.000 |

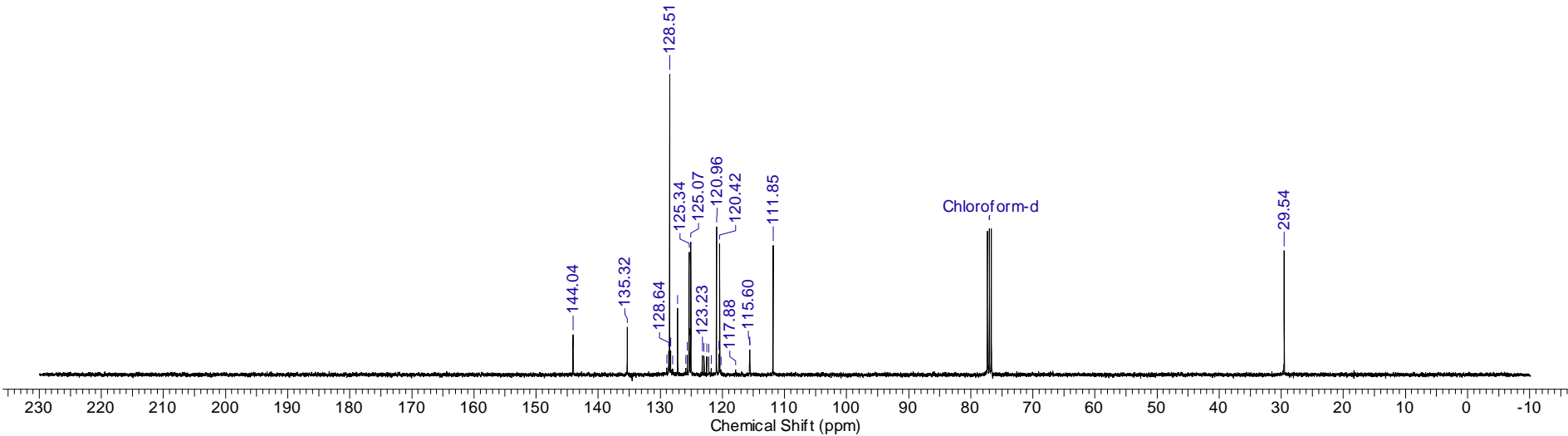
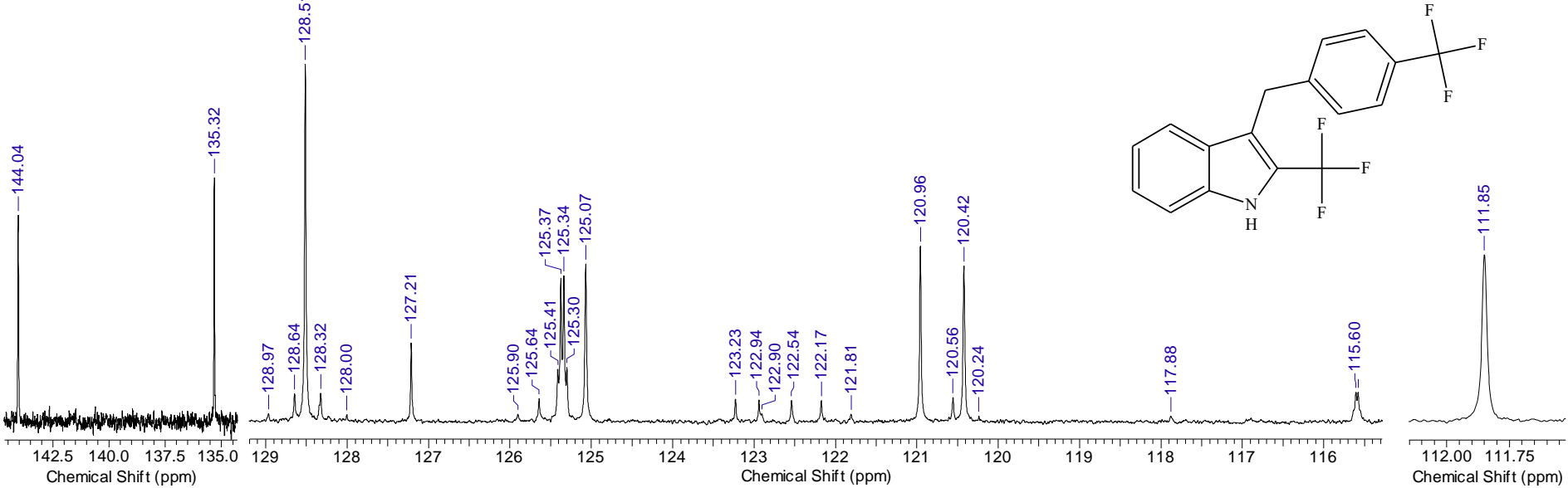
<sup>1</sup>H NMR spectrum of **4e** (400.1 MHz, CDCl<sub>3</sub>)

|                        |          |                        |             |                      |   |                             |
|------------------------|----------|------------------------|-------------|----------------------|---|-----------------------------|
| Acquisition Time (sec) | 1.0000   | Date                   | Nov 25 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.11.25\BM-1803_20191125_01\FLUORINE_01 |                             |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F         | Number of Transients | 16  | Original Points Count 89286 |
| Points Count           | 131072   | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D  |                             |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 20.000      |                      |   |                             |



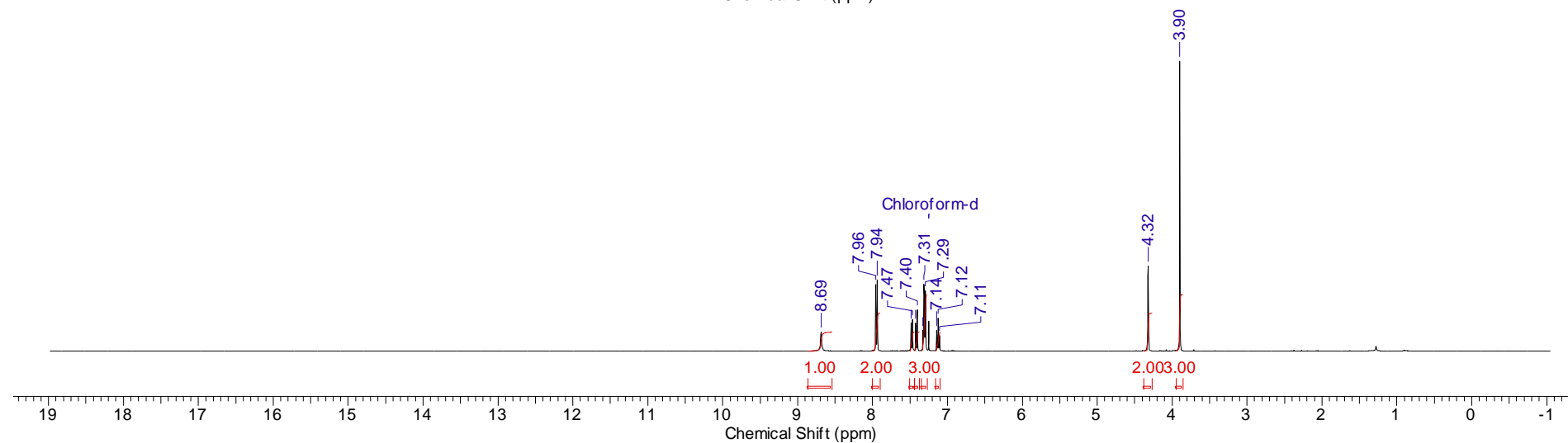
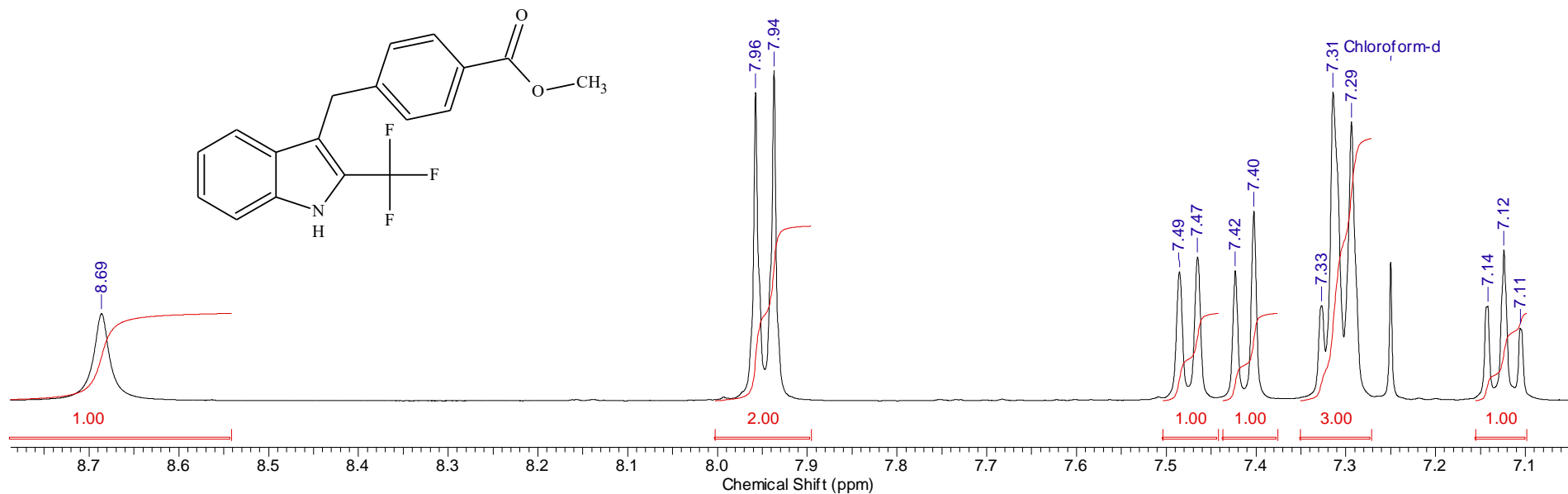
<sup>19</sup>F NMR spectrum of **4e** (376.5 MHz, CDCl<sub>3</sub>)

|                               |  |                              |                      |                               |                      |
|-------------------------------|--|------------------------------|----------------------|-------------------------------|----------------------|
| <b>Acquisition Time (sec)</b> | 0.6783   | <b>Comment</b>               | Imported from UXMNR. | <b>Date</b>                   | 26 Nov 2019 13:12:08 |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2019\11.脛 狙黒BM-1803.C_002001r | <b>Frequency (MHz)</b>       | 100.61               | <b>Nucleus</b>                | <sup>13</sup> C      |
| <b>Number of Transients</b>   | 210  | <b>Original Points Count</b> | 16384                | <b>Points Count</b>           | 131072               |
| <b>Solvent</b>                | CHLOROFORM-D                                     | <b>Sweep Width (Hz)</b>      | 24154.59             | <b>Pulse Sequence</b>         | zgpg30               |
|                               |  |                              |                      | <b>Temperature (degree C)</b> | 27.000               |

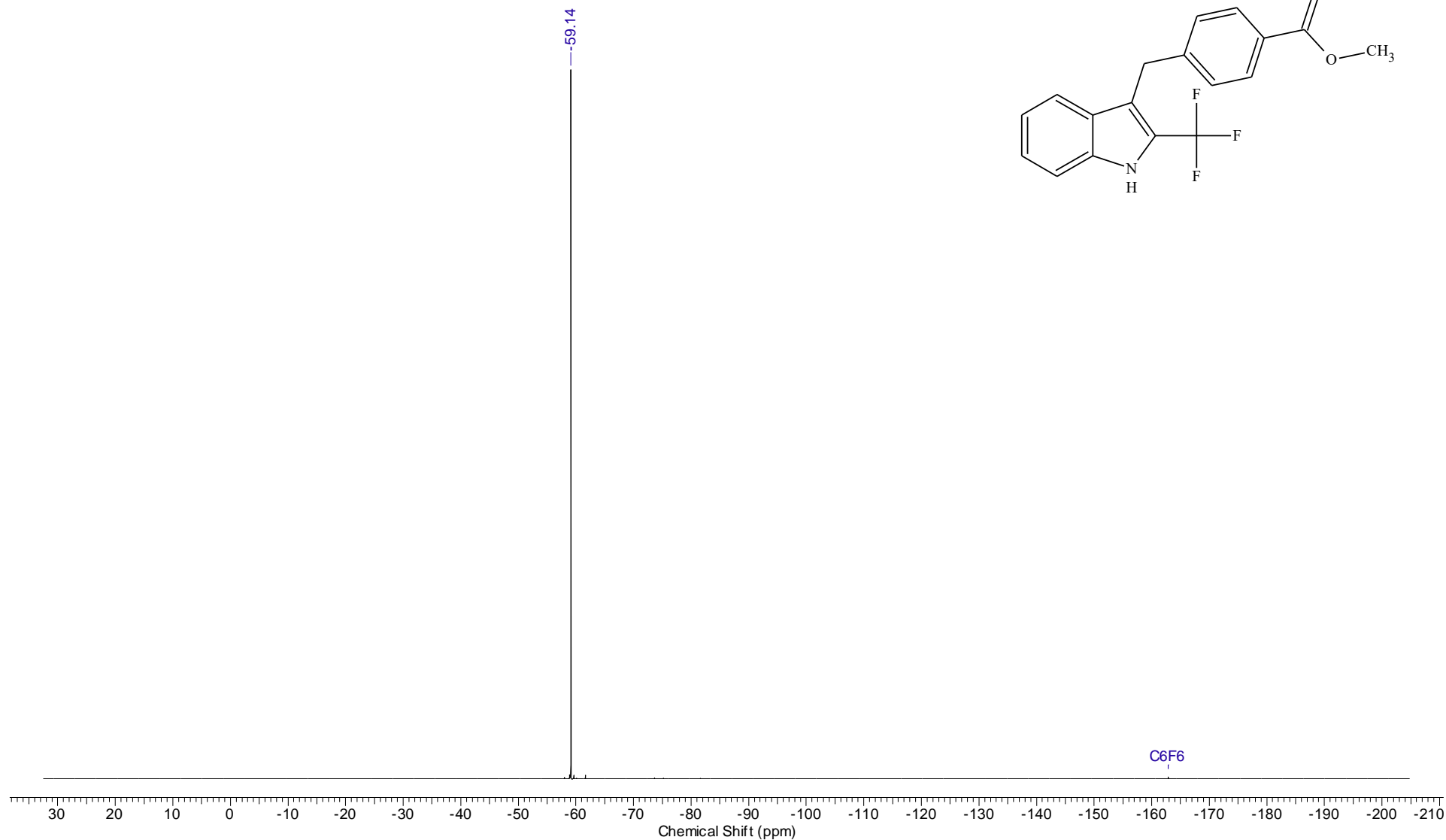
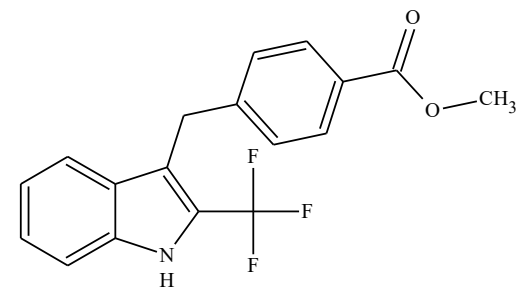


<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4e** (100.6 MHz, CDCl<sub>3</sub>)

|                               |                                     |                               |                      |                       |             |                             |              |
|-------------------------------|-------------------------------------|-------------------------------|----------------------|-----------------------|-------------|-----------------------------|--------------|
| <b>Acquisition Time (sec)</b> | 4.0894                              | <b>Comment</b>                | Imported from UXNMR. |                       | <b>Date</b> | 26 Nov 2019 20:56:52        |              |
| <b>File Name</b>              | C:\DOCS\BM\bm191126\BM-1805_001001r | <b>Frequency (MHz)</b>        | 400.13               | <b>Nucleus</b>        | 1H          | <b>Number of Transients</b> | 8            |
| <b>Original Points Count</b>  | 32768                               | <b>Points Count</b>           | 131072               | <b>Pulse Sequence</b> | zg30        | <b>Solvent</b>              | CHLOROFORM-D |
| <b>Sweep Width (Hz)</b>       | 8012.82                             | <b>Temperature (degree C)</b> | 27.000               |                       |             |                             |              |

<sup>1</sup>H NMR spectrum of **4f** (400.1 MHz, CDCl<sub>3</sub>)

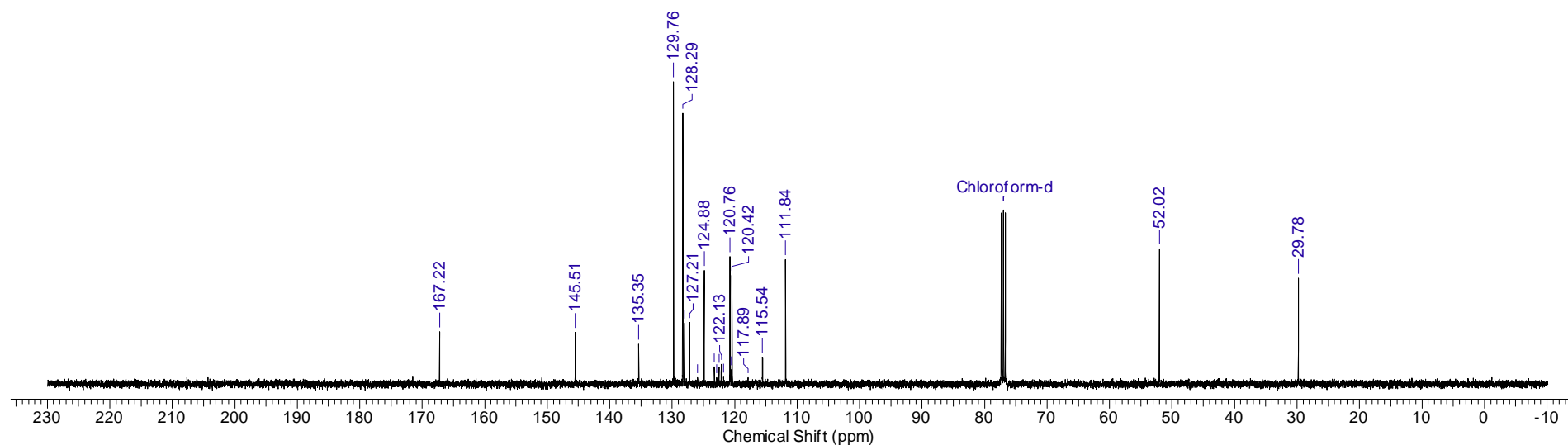
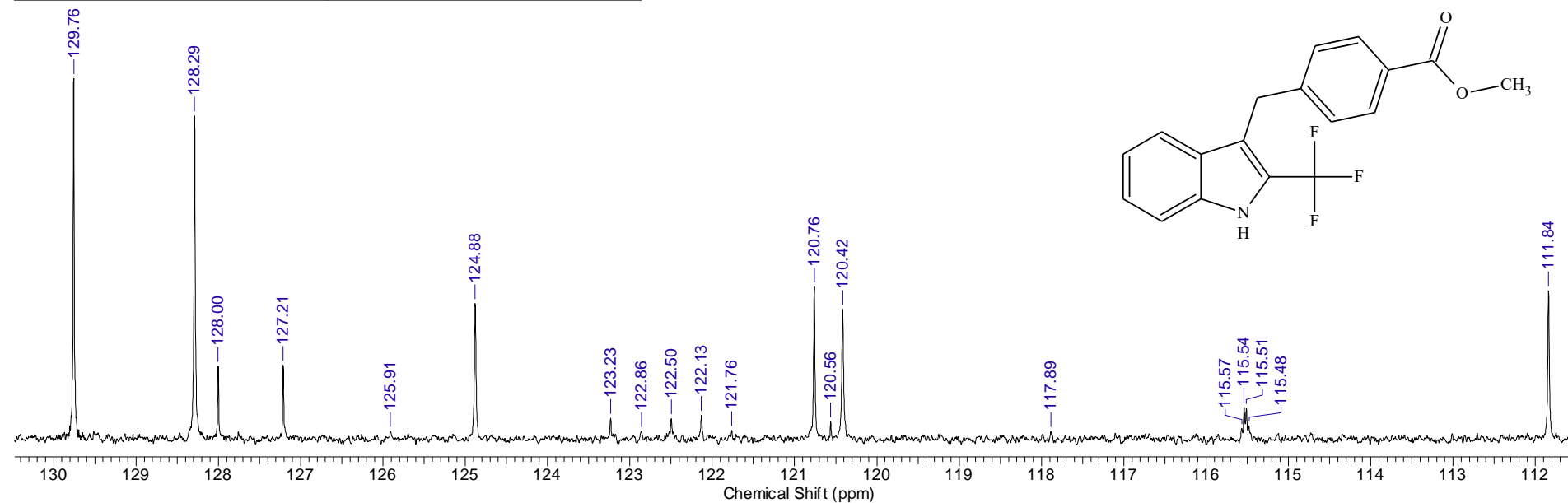
|                        |          |                        |             |                      |  |                             |
|------------------------|----------|------------------------|-------------|----------------------|--|-----------------------------|
| Acquisition Time (sec) | 0.7340   | Date                   | Nov 26 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.11.26\bm1805-f_20191126_01\FLUORINE_01 |                             |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F         | Number of Transients | 100  | Original Points Count 65536 |
| Points Count           | 65536    | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D   |                             |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 20.000      |                      |  |                             |



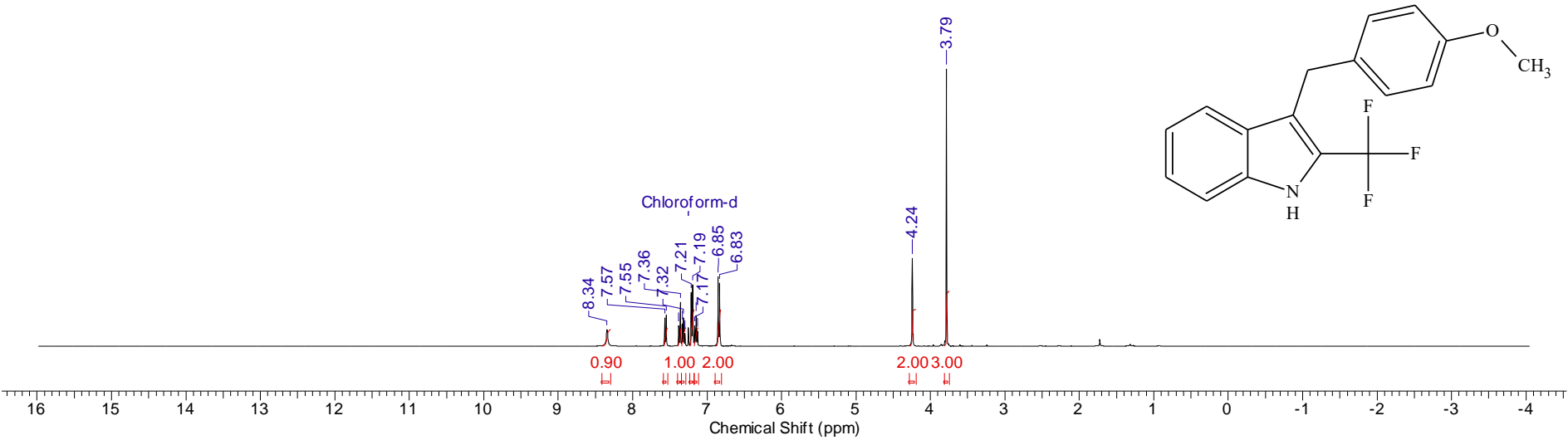
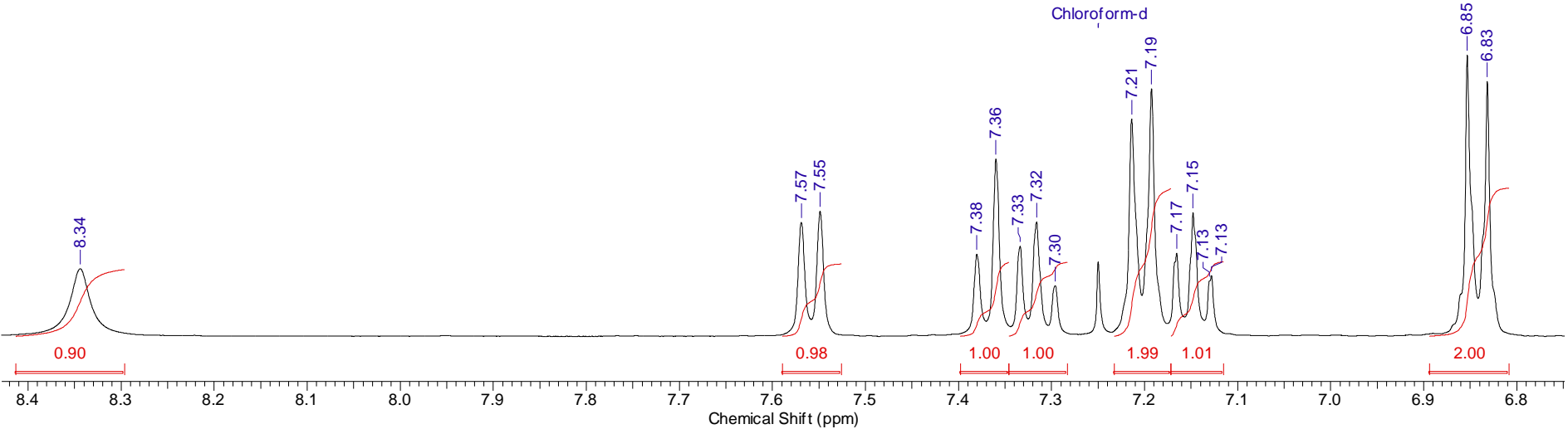
$^{19}\text{F}$  NMR spectrum of **4f** (376.5 MHz,  $\text{CDCl}_3$ )



|                               |                                     |                               |                      |                       |             |                             |              |
|-------------------------------|-------------------------------------|-------------------------------|----------------------|-----------------------|-------------|-----------------------------|--------------|
| <b>Acquisition Time (sec)</b> | 0.6783                              | <b>Comment</b>                | Imported from UXNMR. |                       | <b>Date</b> | 26 Nov 2019 21:00:54        |              |
| <b>File Name</b>              | C:\DOCS\BM\bm191126\BM-1805_002001r | <b>Frequency (MHz)</b>        | 100.61               | <b>Nucleus</b>        | 13C         | <b>Number of Transients</b> | 72           |
| <b>Original Points Count</b>  | 16384                               | <b>Points Count</b>           | 131072               | <b>Pulse Sequence</b> | zgpg30      | <b>Solvent</b>              | CHLOROFORM-D |
| <b>Sweep Width (Hz)</b>       | 24154.59                            | <b>Temperature (degree C)</b> | 27.000               |                       |             |                             |              |

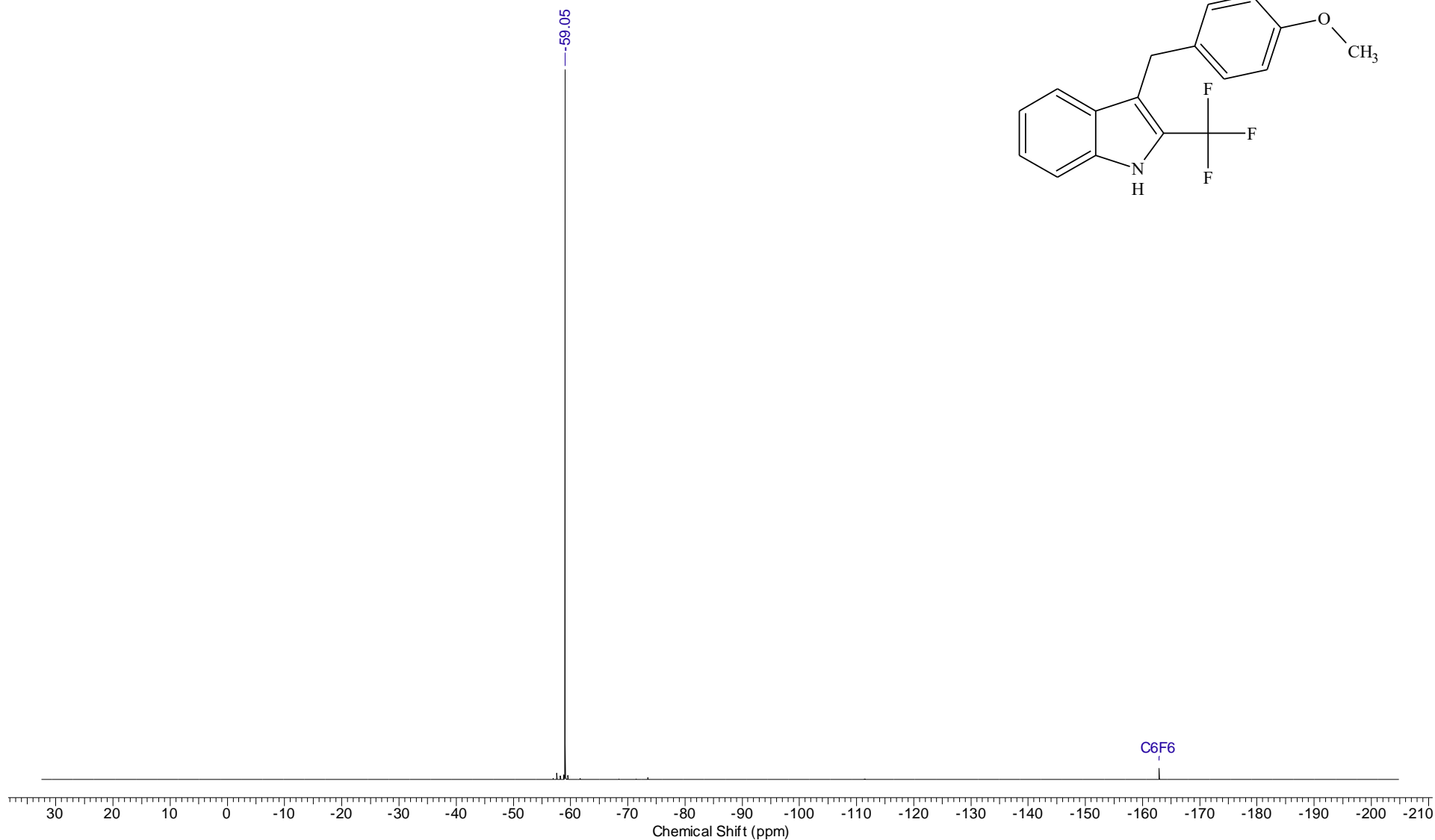
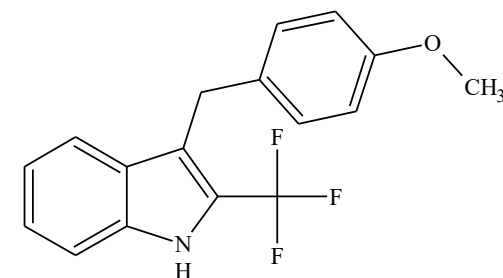
 $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4f** (100.6 MHz,  $\text{CDCl}_3$ )

|                        |  |                      |              |                       |                      |                  |                      |
|------------------------|--|----------------------|--------------|-----------------------|----------------------|------------------|----------------------|
| Acquisition Time (sec) | 4.0894   | Comment              |              |                       | Imported from Uxnmr. | Date             | 11 Oct 2019 15:35:34 |
| File Name              | C:\DOCS\OUTPUT_301\201910.舘? 狢黒BM-1732-1.H_001001r |                      |              |                       |                      | Frequency (MHz)  | 400.13               |
| Nucleus                | 1H   | Number of Transients | 4            | Original Points Count | 32768                | Points Count     | 131072               |
| Pulse Sequence         | zg30   | Solvent              | CHLOROFORM-D |                       |                      | Sweep Width (Hz) | 8012.82              |
| Temperature (degree C) | 27.000   |                      |              |                       |                      |                  |                      |



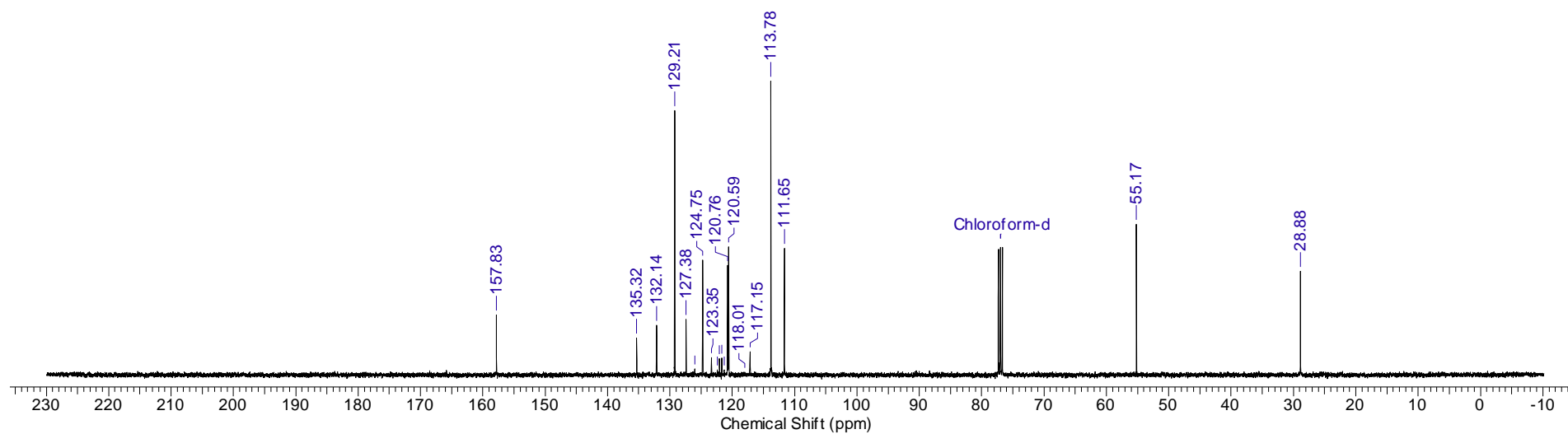
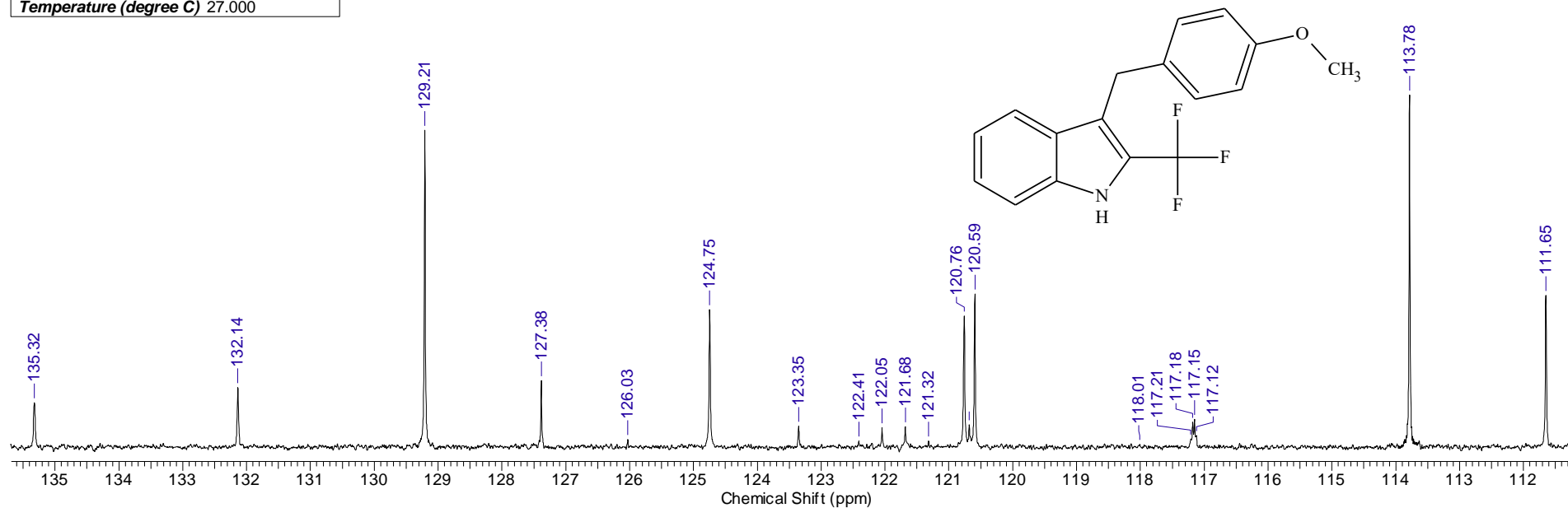
<sup>1</sup>H NMR spectrum of **4g** (400.1 MHz, CDCl<sub>3</sub>)

|                        |          |                        |             |                      |   |                              |
|------------------------|----------|------------------------|-------------|----------------------|---|------------------------------|
| Acquisition Time (sec) | 2.0000   | Date                   | Oct 14 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.10.14\BM-1732-1_20191014_01\FLUORINE_01 |                              |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F         | Number of Transients | 16  | Original Points Count 178571 |
| Points Count           | 262144   | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D  |                              |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 30.000      |                      |   |                              |

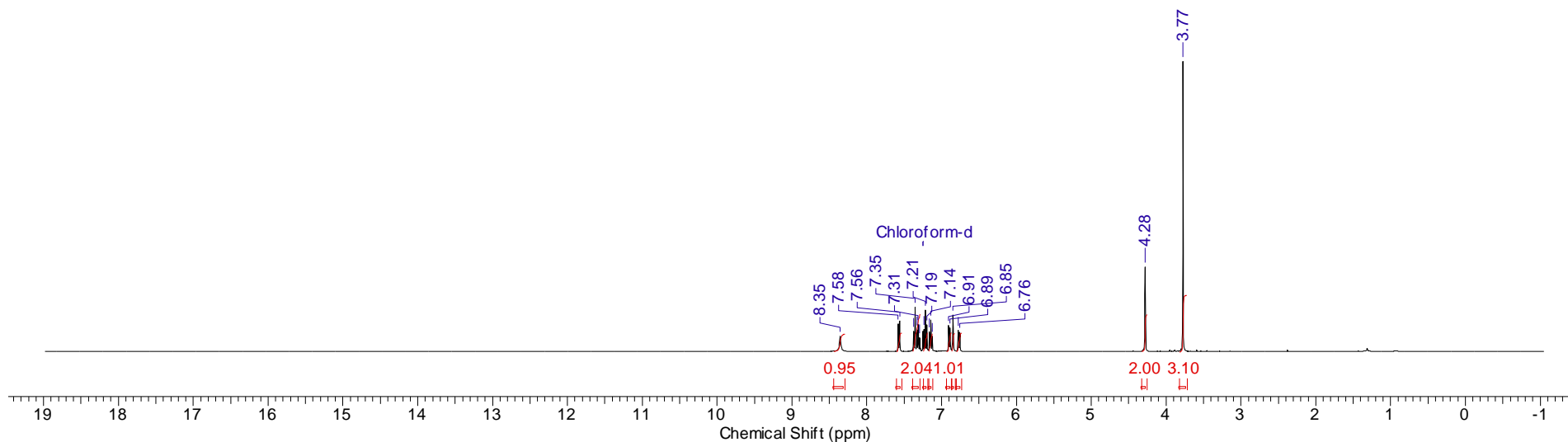
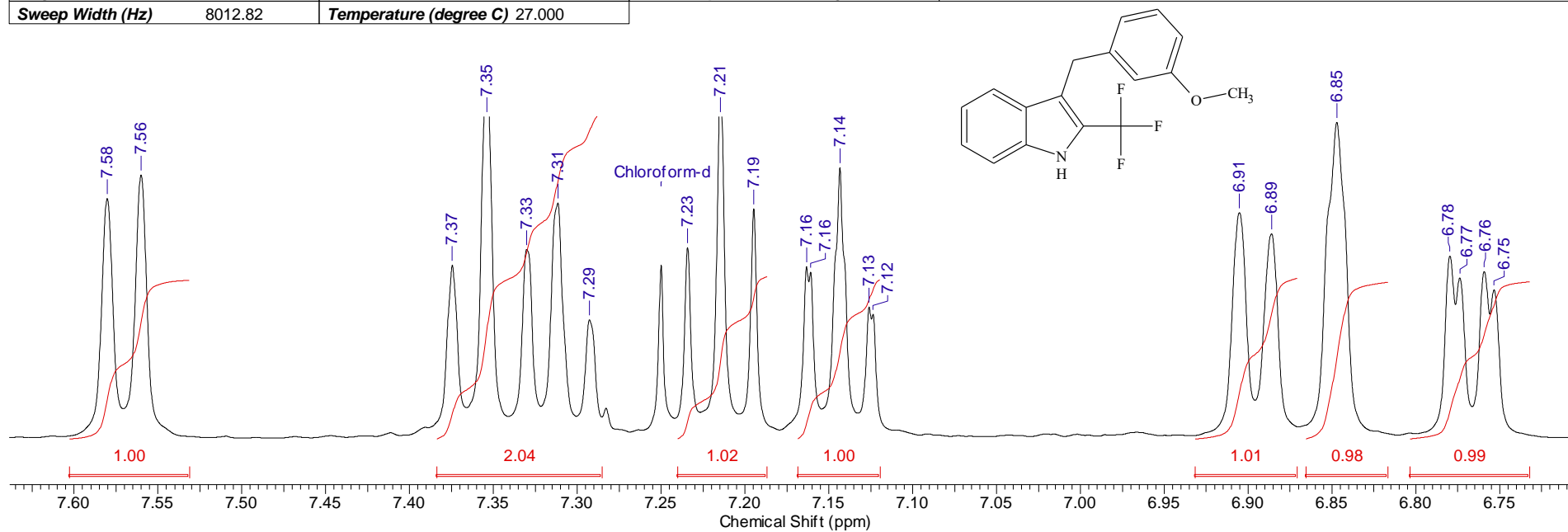


<sup>19</sup>F NMR spectrum of **4g** (376.5 MHz, CDCl<sub>3</sub>)

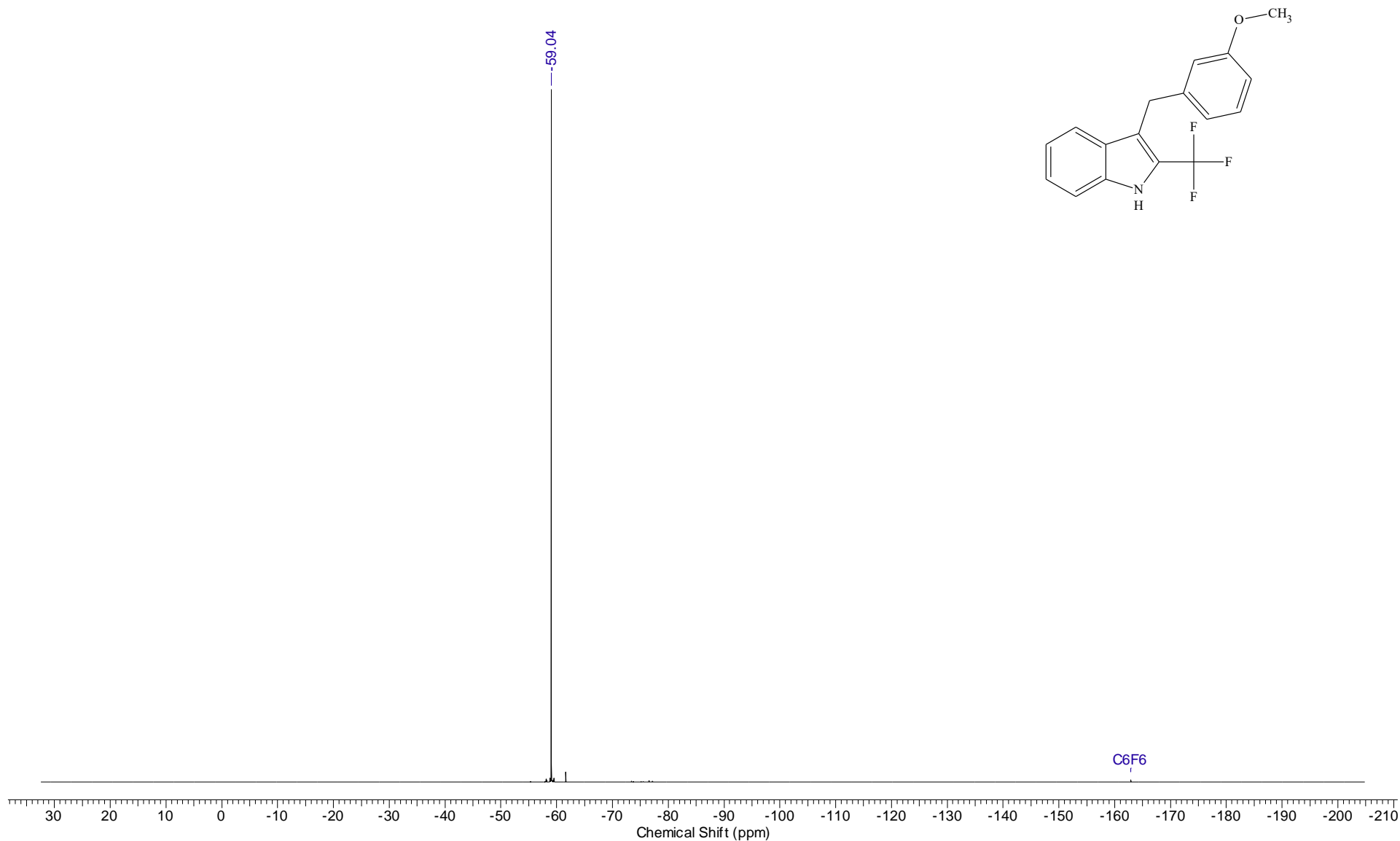
|                               |   |                             |                      |                              |                      |
|-------------------------------|---|-----------------------------|----------------------|------------------------------|----------------------|
| <b>Acquisition Time (sec)</b> | 0.6783  | <b>Comment</b>              | Imported from UXNMR. | <b>Date</b>                  | 11 Oct 2019 15:41:16 |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2019\10.锐? 狙黑BM-1732-1.C_002001r |                             |                      | <b>Frequency (MHz)</b>       | 100.61               |
| <b>Nucleus</b>                | <sup>13</sup> C                                     | <b>Number of Transients</b> | 137                  | <b>Original Points Count</b> | 16384                |
| <b>Pulse Sequence</b>         | zgpg30  | <b>Solvent</b>              | CHLOROFORM-D         | <b>Points Count</b>          | 131072               |
| <b>Temperature (degree C)</b> | 27.000  |                             |                      | <b>Sweep Width (Hz)</b>      | 24154.59             |

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4g** (100.6 MHz, CDCl<sub>3</sub>)

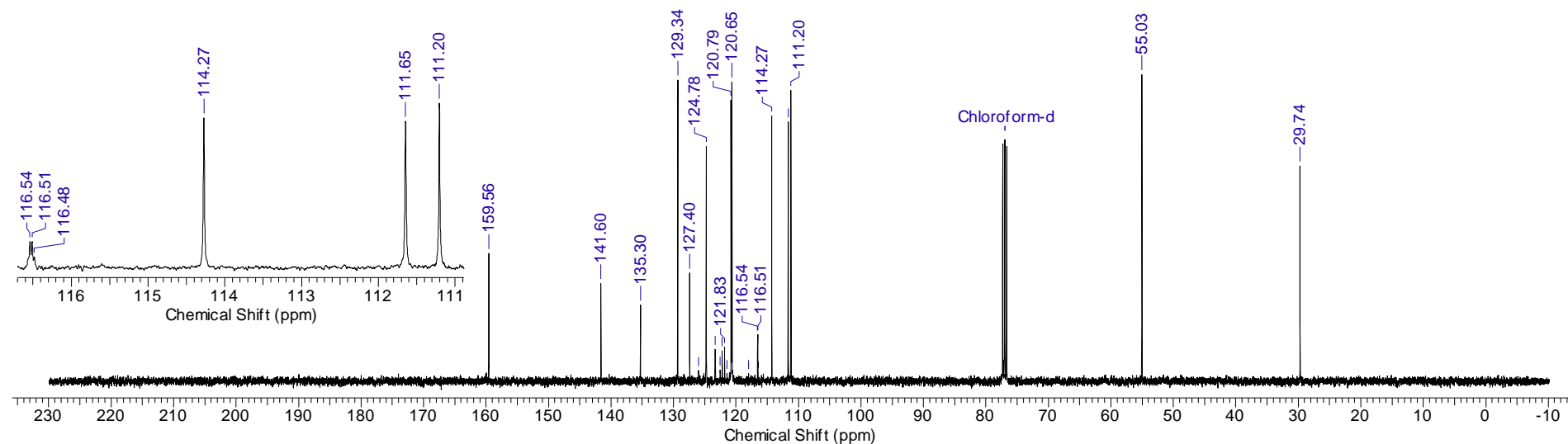
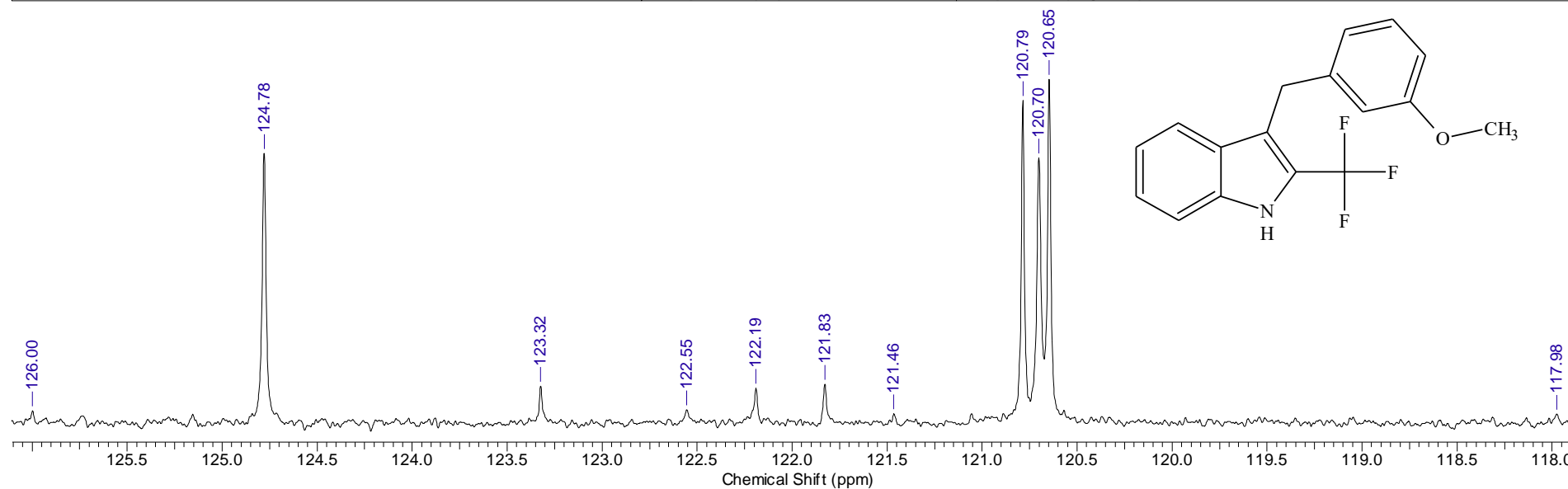
|                               |                                     |                               |                      |                       |             |                             |              |
|-------------------------------|-------------------------------------|-------------------------------|----------------------|-----------------------|-------------|-----------------------------|--------------|
| <b>Acquisition Time (sec)</b> | 4.0894                              | <b>Comment</b>                | Imported from UXNMR. |                       | <b>Date</b> | 26 Nov 2019 21:03:36        |              |
| <b>File Name</b>              | C:\DOCS\BM\bm191126\BM-1798_001001r | <b>Frequency (MHz)</b>        | 400.13               | <b>Nucleus</b>        | 1H          | <b>Number of Transients</b> | 8            |
| <b>Original Points Count</b>  | 32768                               | <b>Points Count</b>           | 131072               | <b>Pulse Sequence</b> | zg30        | <b>Solvent</b>              | CHLOROFORM-D |
| <b>Sweep Width (Hz)</b>       | 8012.82                             | <b>Temperature (degree C)</b> | 27.000               |                       |             |                             |              |

<sup>1</sup>H NMR spectrum of **4h** (400.1 MHz, CDCl<sub>3</sub>)

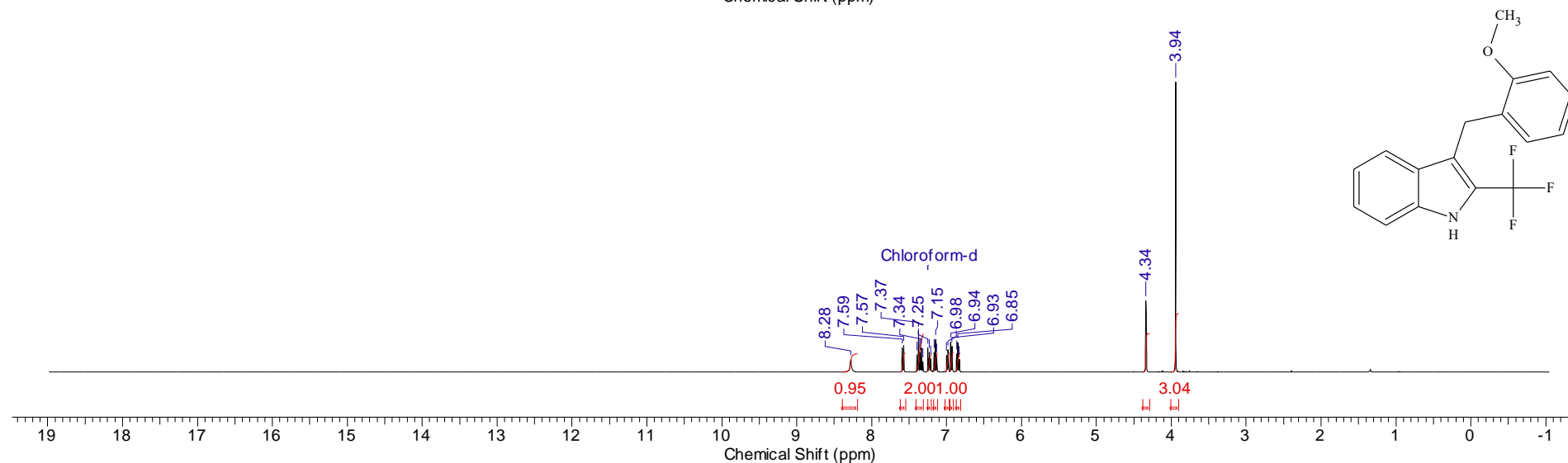
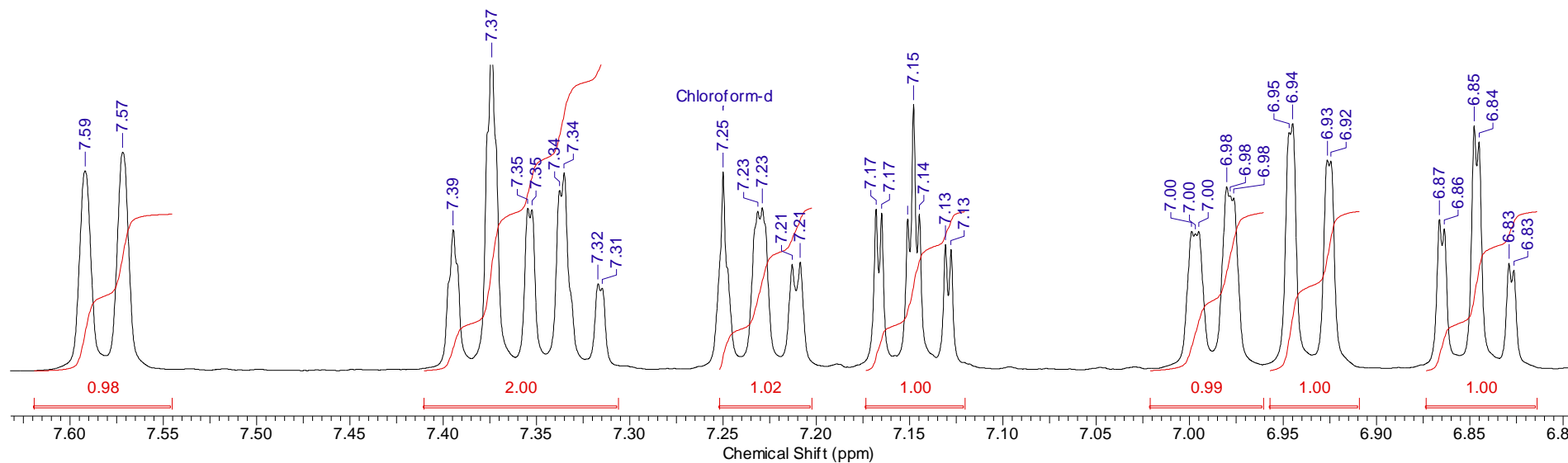
|                        |   |                      |                              |                       |                 |                        |        |
|------------------------|---|----------------------|------------------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 1.0000  | Comment              | STANDARD FLUORINE PARAMETERS |                       | Date            | Nov 25 2019            |        |
| File Name              | C:\DOCS\OUTPUT_301\F19\2019.11.25\BM-1798_20191125_01\FLUORINE_01 |                      |                              |                       | Frequency (MHz) | 376.31                 |        |
| Nucleus                | 19F   | Number of Transients | 16                           | Original Points Count | 89286           | Points Count           | 131072 |
| Pulse Sequence         | s2pul   | Solvent              | CHLOROFORM-D                 | Sweep Width (Hz)      | 89285.71        | Temperature (degree C) | 20.000 |

<sup>19</sup>F NMR spectrum of **4h** (376.5 MHz, CDCl<sub>3</sub>)

|                        |                                     |                       |                      |              |                        |                      |        |
|------------------------|-------------------------------------|-----------------------|----------------------|--------------|------------------------|----------------------|--------|
| Acquisition Time (sec) | 0.6783                              | Comment               | Imported from UXMNR. |              | Date                   | 26 Nov 2019 21:09:40 |        |
| File Name              | C:\DOCS\BM\bm191126\BM-1798_002001r |                       | Frequency (MHz)      | 100.61       | Nucleus                | 13C                  |        |
| Number of Transients   | 136                                 | Original Points Count | 16384                | Points Count | 131072                 | Pulse Sequence       | zgpg30 |
| Solvent                | CHLOROFORM-D                        |                       | Sweep Width (Hz)     | 24154.59     | Temperature (degree C) | 27.000               |        |

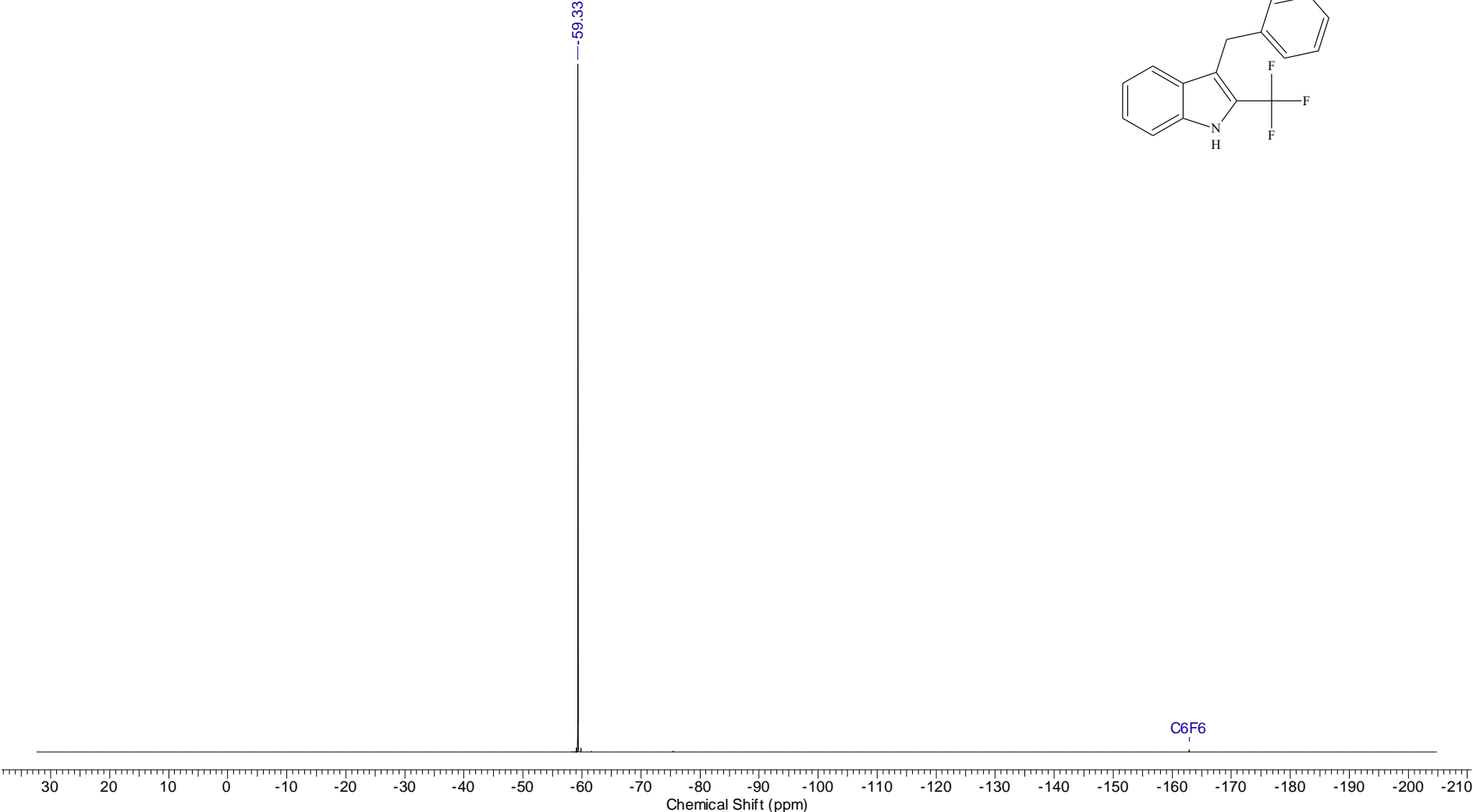
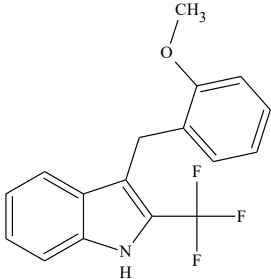
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4h** (100.6 MHz, CDCl<sub>3</sub>)

|                        |  |                      |                      |                       |                 |                        |        |
|------------------------|--|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UXMNR. |                       | Date            | 27 Nov 2019 17:53:40   |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙鼎BM-1799.H_001001r |                      |                      |                       | Frequency (MHz) | 400.13                 |        |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768           | Points Count           | 131072 |
| Pulse Sequence         | zg30   | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 8012.82         | Temperature (degree C) | 27.000 |

<sup>1</sup>H NMR spectrum of **4i** (400.1 MHz, CDCl<sub>3</sub>)

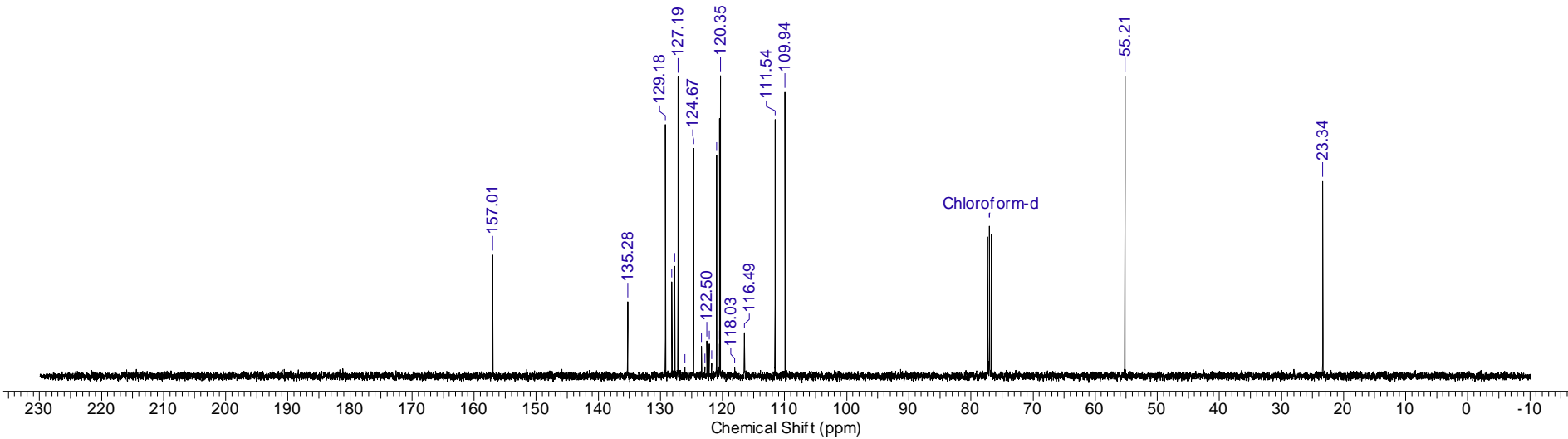
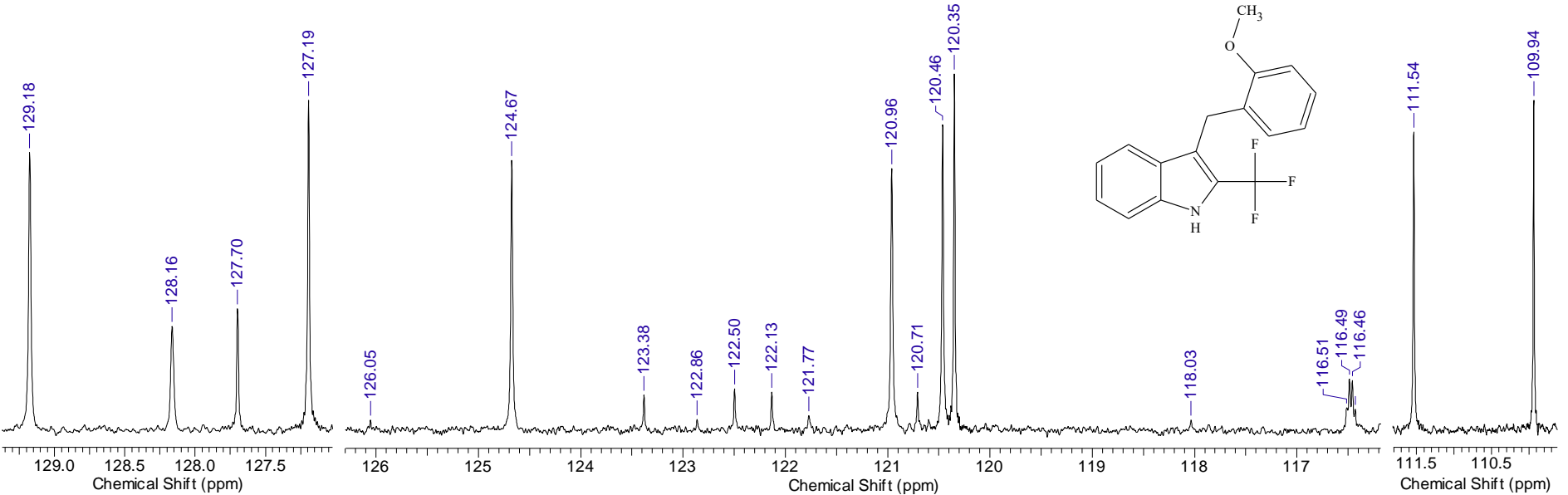


|                        |          |                        |             |                      |   |                             |
|------------------------|----------|------------------------|-------------|----------------------|---|-----------------------------|
| Acquisition Time (sec) | 1.0000   | Date                   | Nov 25 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.11.25\BM-1799_20191125_01\FLUORINE_01 |                             |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F         | Number of Transients | 16  | Original Points Count 89286 |
| Points Count           | 131072   | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D  |                             |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 20.000      |                      |   |                             |



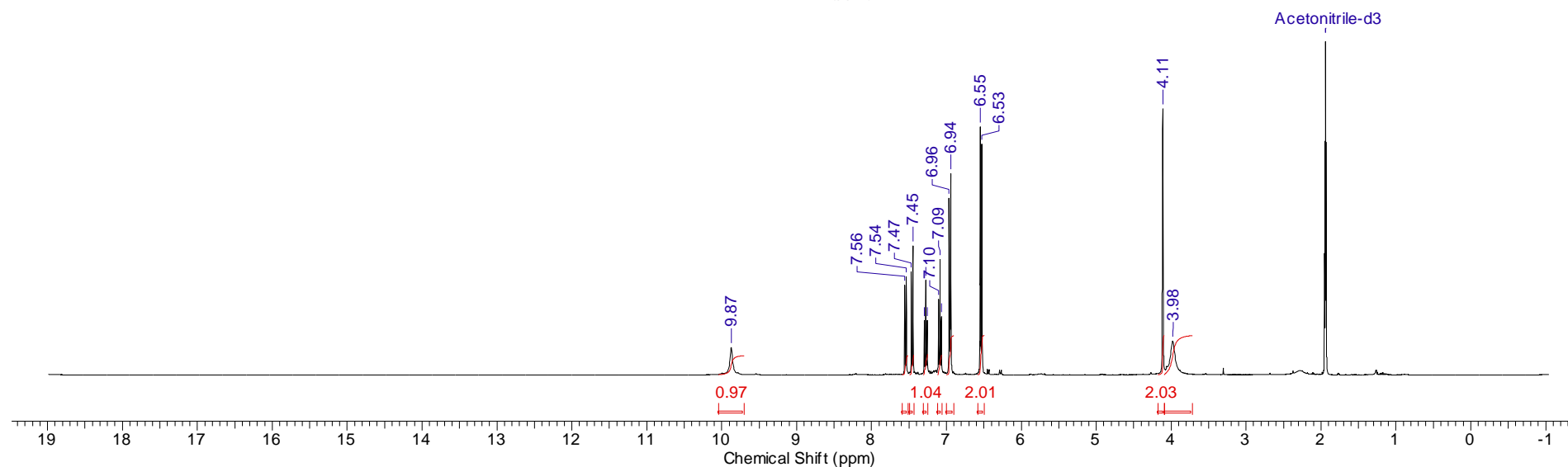
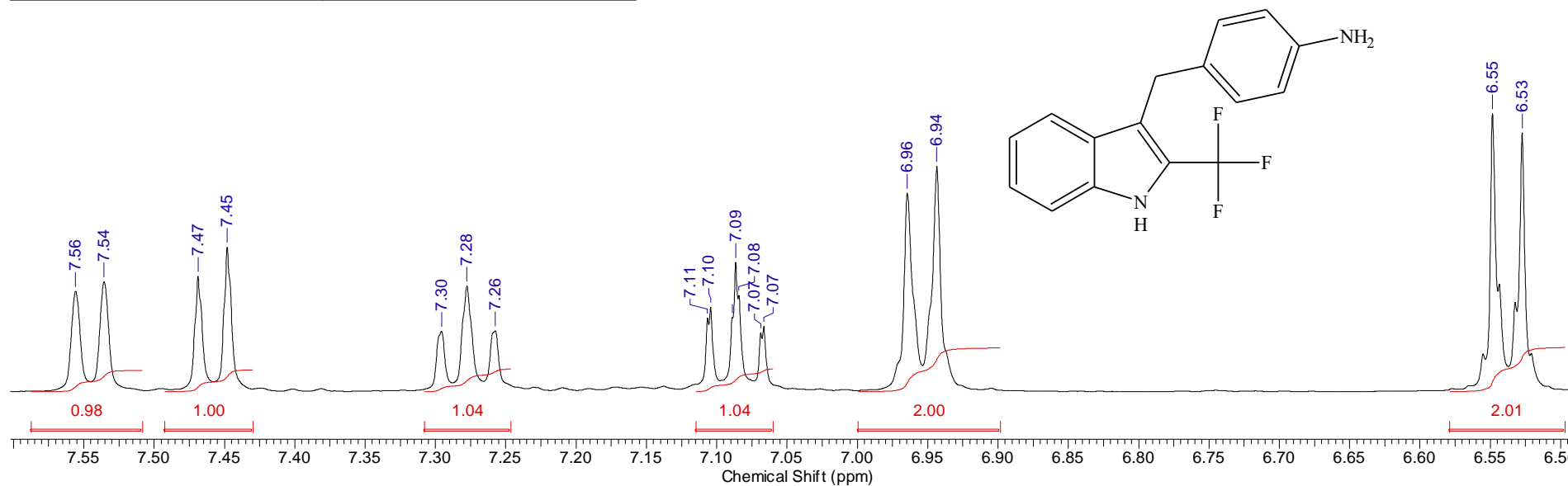
<sup>19</sup>F NMR spectrum of **4i** (376.5 MHz, CDCl<sub>3</sub>)

|                        |   |                       |                      |  |                        |                      |  |
|------------------------|---|-----------------------|----------------------|--|------------------------|----------------------|--|
| Acquisition Time (sec) | 0.6783  | Comment               | Imported from UXMNR. |  | Date                   | 27 Nov 2019 17:57:52 |  |
| File Name              | C:\DOCS\OUTPUT_301\2019\11. 羧 狙黒BM-1799.C_002001r | Frequency (MHz)       | 100.61               |  | Nucleus                | 13C                  |  |
| Number of Transients   | 98  | Original Points Count | 16384                |  | Pulse Sequence         | zgpg30               |  |
| Solvent                | CHLOROFORM-D                                      | Sweep Width (Hz)      | 24154.59             |  | Temperature (degree C) | 27.000               |  |

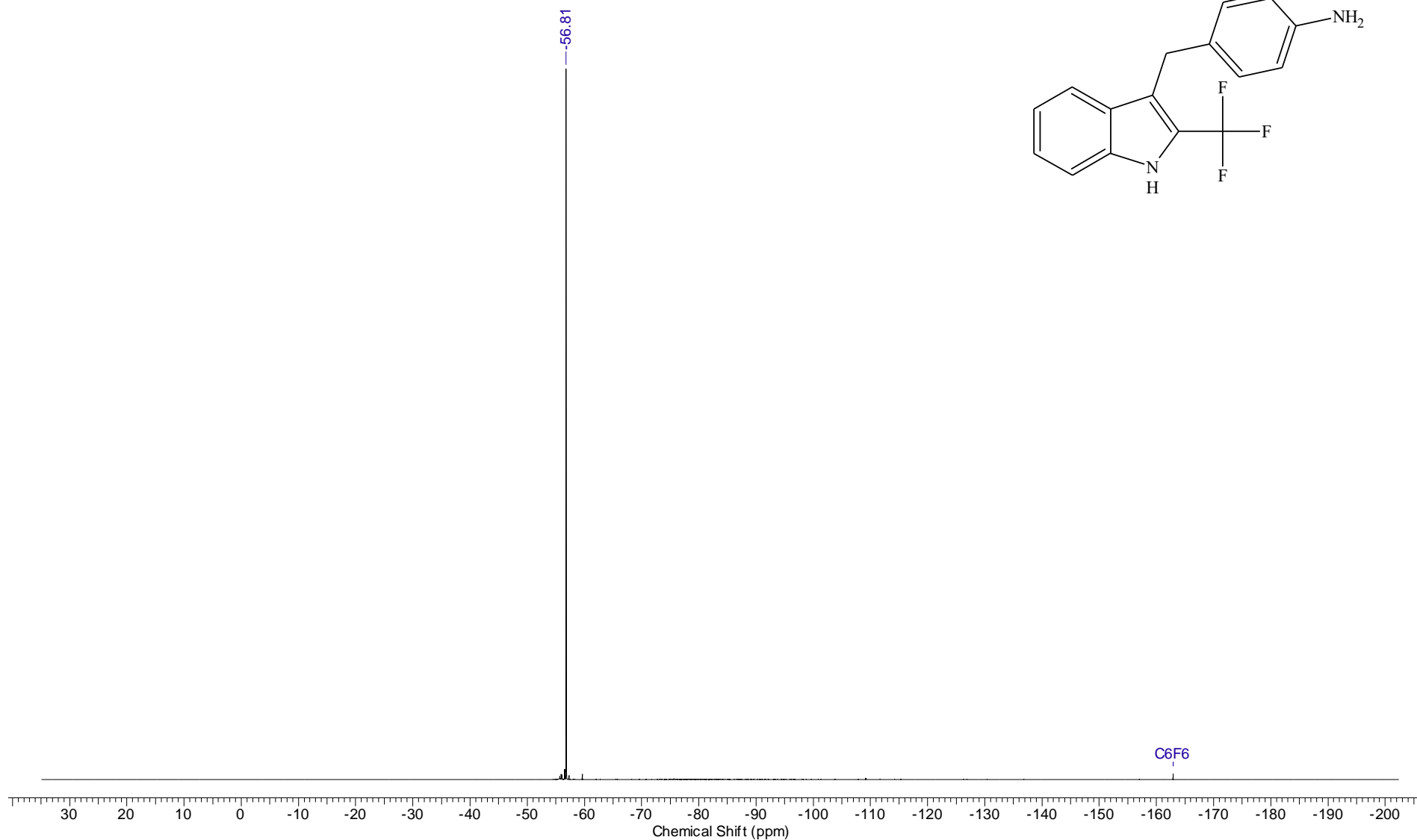
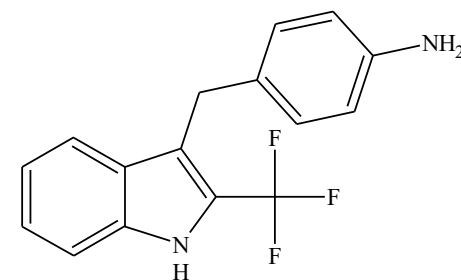


<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of 4i (100.6 MHz, CDCl<sub>3</sub>)

|                               |  |                               |                      |                       |             |                             |                 |
|-------------------------------|--|-------------------------------|----------------------|-----------------------|-------------|-----------------------------|-----------------|
| <b>Acquisition Time (sec)</b> | 4.0894                                 | <b>Comment</b>                | Imported from UXNMR. |                       | <b>Date</b> | 14 Dec 2019 13:50:26        |                 |
| <b>File Name</b>              | C:\DOCS\BM\BM-1825-p\BM-1825-p_001001r | <b>Frequency (MHz)</b>        | 400.13               | <b>Nucleus</b>        | 1H          | <b>Number of Transients</b> | 8               |
| <b>Original Points Count</b>  | 32768                                  | <b>Points Count</b>           | 131072               | <b>Pulse Sequence</b> | zg30        | <b>Solvent</b>              | ACETONITRILE-D3 |
| <b>Sweep Width (Hz)</b>       | 8012.82                                | <b>Temperature (degree C)</b> | 27.000               |                       |             |                             |                 |

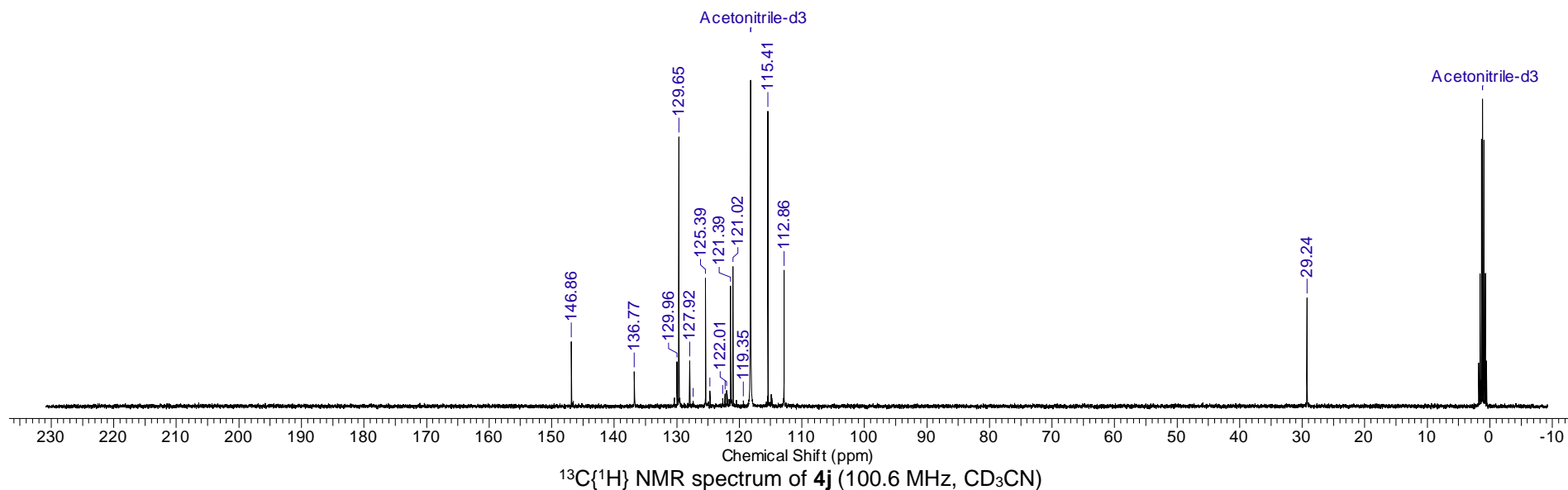
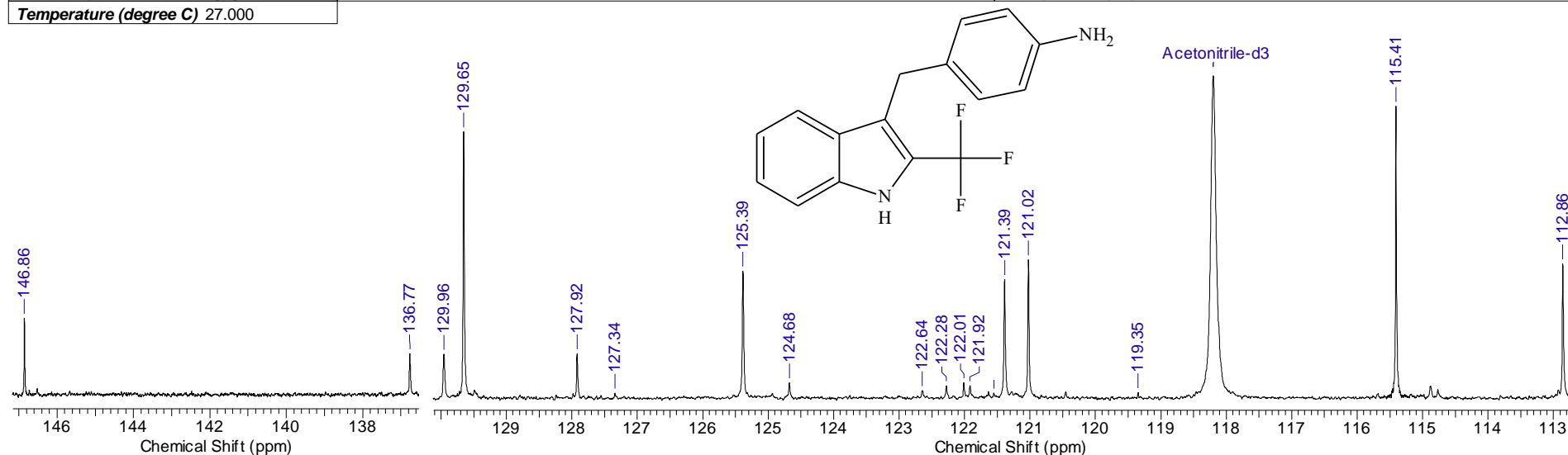
<sup>1</sup>H NMR spectrum of **4j** (400.1 MHz, CDCl<sub>3</sub>)

|                        |          |                        |             |                      |   |                              |
|------------------------|----------|------------------------|-------------|----------------------|---|------------------------------|
| Acquisition Time (sec) | 2.0000   | Date                   | Dec 16 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.12.16\BM-1825-p_20191216_01\FLUORINE_01 |                              |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F         | Number of Transients | 16  | Original Points Count 178571 |
| Points Count           | 262144   | Pulse Sequence         | s2pul       | Solvent              | ACETONITRILE-D3   |                              |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 30.000      |                      |   |                              |



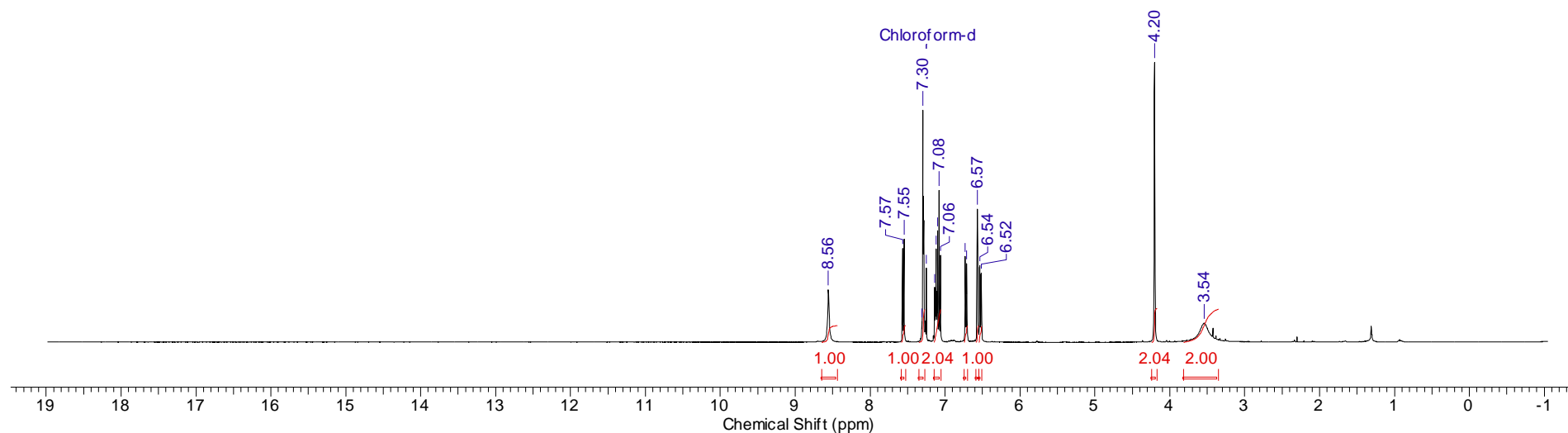
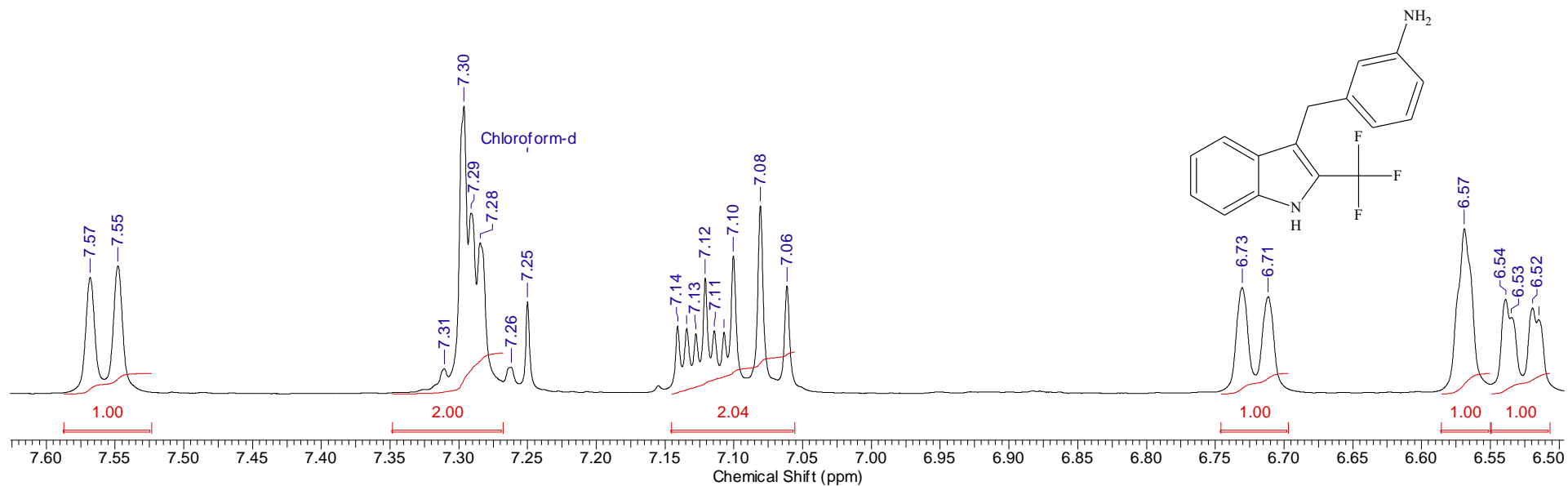
<sup>19</sup>F NMR spectrum of **4j** (376.5 MHz CDCl<sub>3</sub>)

|                        |  |                      |                      |                       |       |                  |                      |        |
|------------------------|--|----------------------|----------------------|-----------------------|-------|------------------|----------------------|--------|
| Acquisition Time (sec) | 0.6783   | Comment              | Imported from UXNMR. |                       |       | Date             | 12 Dec 2019 13:00:36 |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\12.溴吡喹酮BM-1825.C_002001r |                      |                      |                       |       |                  | Frequency (MHz)      | 100.61 |
| Nucleus                | 13C  | Number of Transients | 233                  | Original Points Count | 16384 | Points Count     | 131072               |        |
| Pulse Sequence         | zgpg30   | Solvent              | CHLOROFORM-D         |                       |       | Sweep Width (Hz) | 24154.59             |        |
| Temperature (degree C) | 27.000   |                      |                      |                       |       |                  |                      |        |

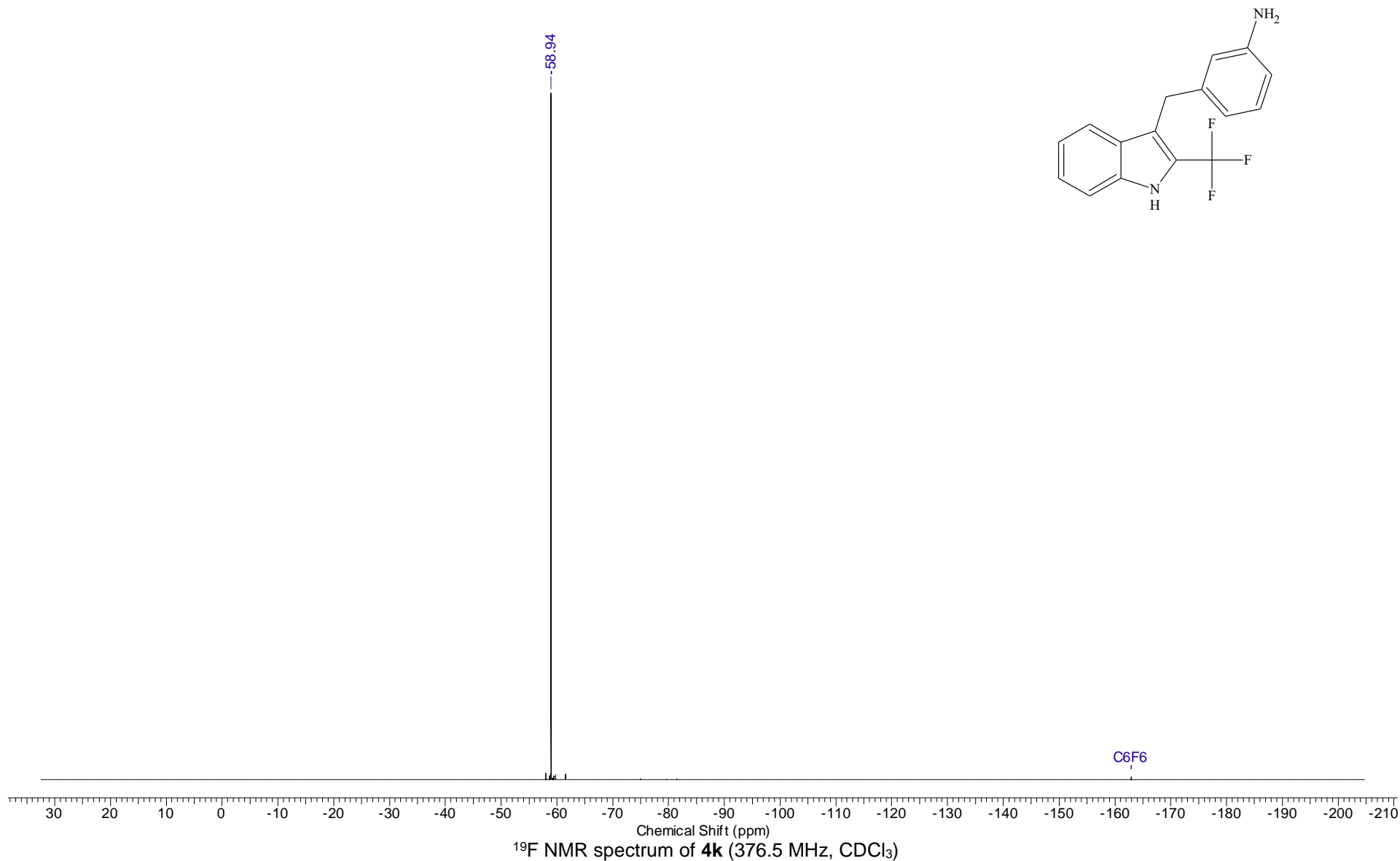


<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4j** (100.6 MHz, CD<sub>3</sub>CN)

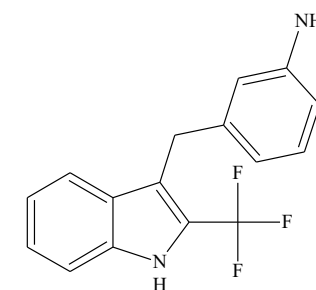
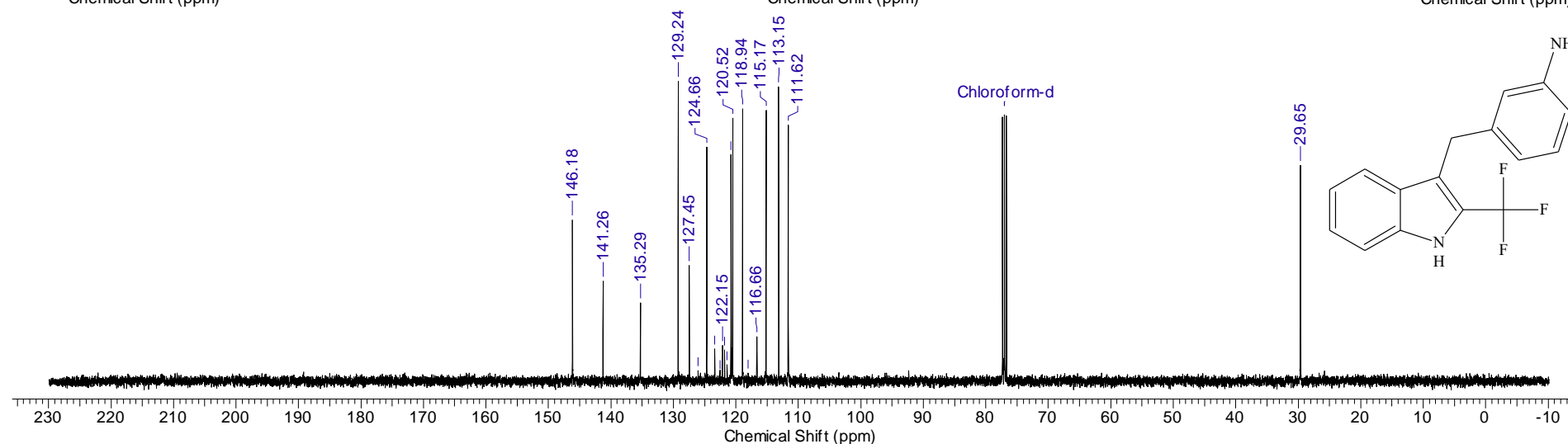
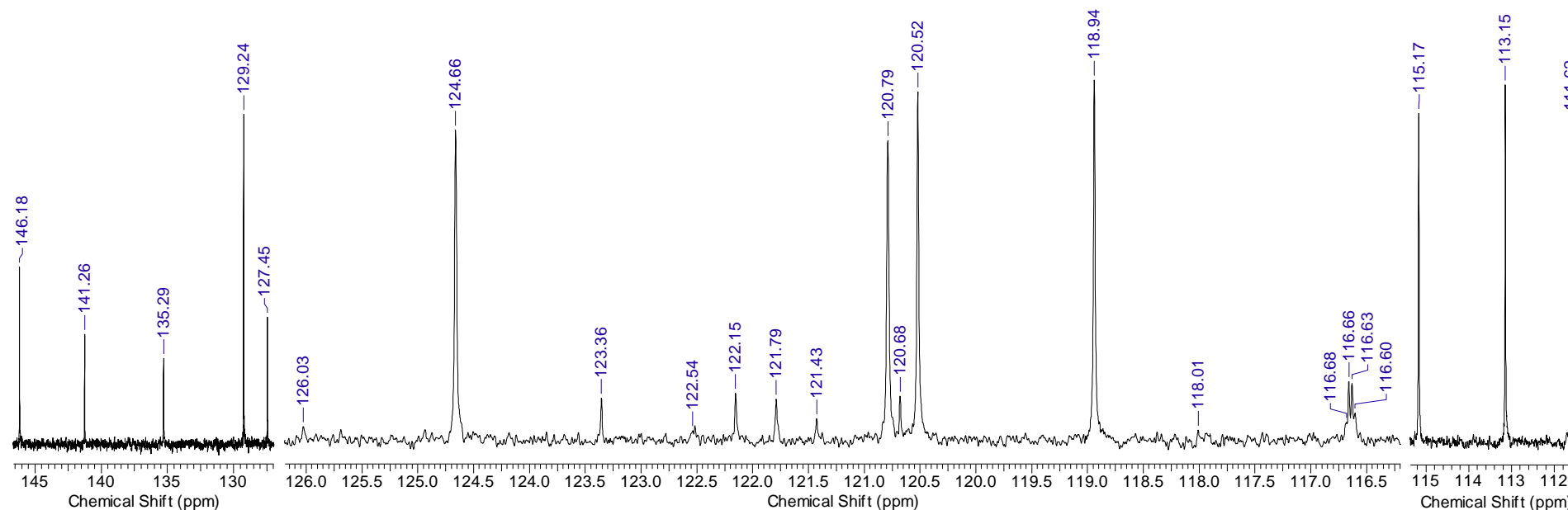
|                        |  |                      |                      |                       |       |                  |                      |
|------------------------|--|----------------------|----------------------|-----------------------|-------|------------------|----------------------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UXNMR. |                       |       | Date             | 29 Nov 2019 15:39:34 |
| File Name              | C:\DOCS\OUTPUT_301\2019\11\鼠狙BM-1804.H_001001r |                      |                      |                       |       | Frequency (MHz)  | 400.13               |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768 | Points Count     | 131072               |
| Pulse Sequence         | zg30   | Solvent              | CHLOROFORM-D         |                       |       | Sweep Width (Hz) | 8012.82              |
| Temperature (degree C) | 27.000   |                      |                      |                       |       |                  |                      |

<sup>1</sup>H NMR spectrum of **4k** (400.1 MHz, CDCl<sub>3</sub>)

|                        |          |                        |             |                      |   |                             |
|------------------------|----------|------------------------|-------------|----------------------|---|-----------------------------|
| Acquisition Time (sec) | 1.0000   | Date                   | Nov 29 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.11.29\BM-1804_20191129_01\FLUORINE_01 |                             |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F         | Number of Transients | 16  | Original Points Count 89286 |
| Points Count           | 131072   | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D  |                             |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 30.000      |                      |   |                             |

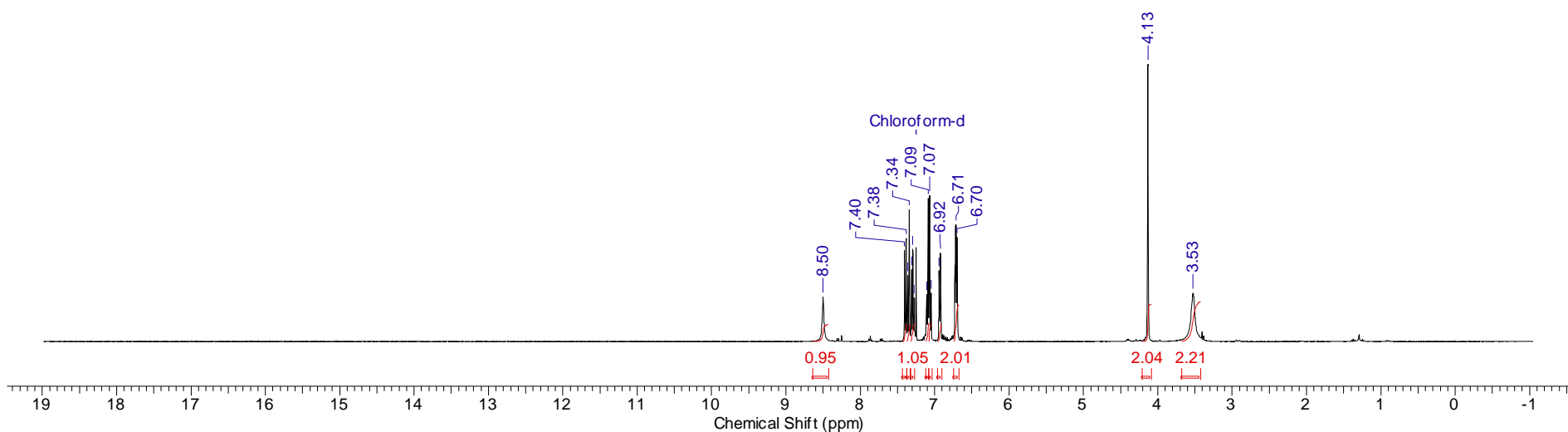
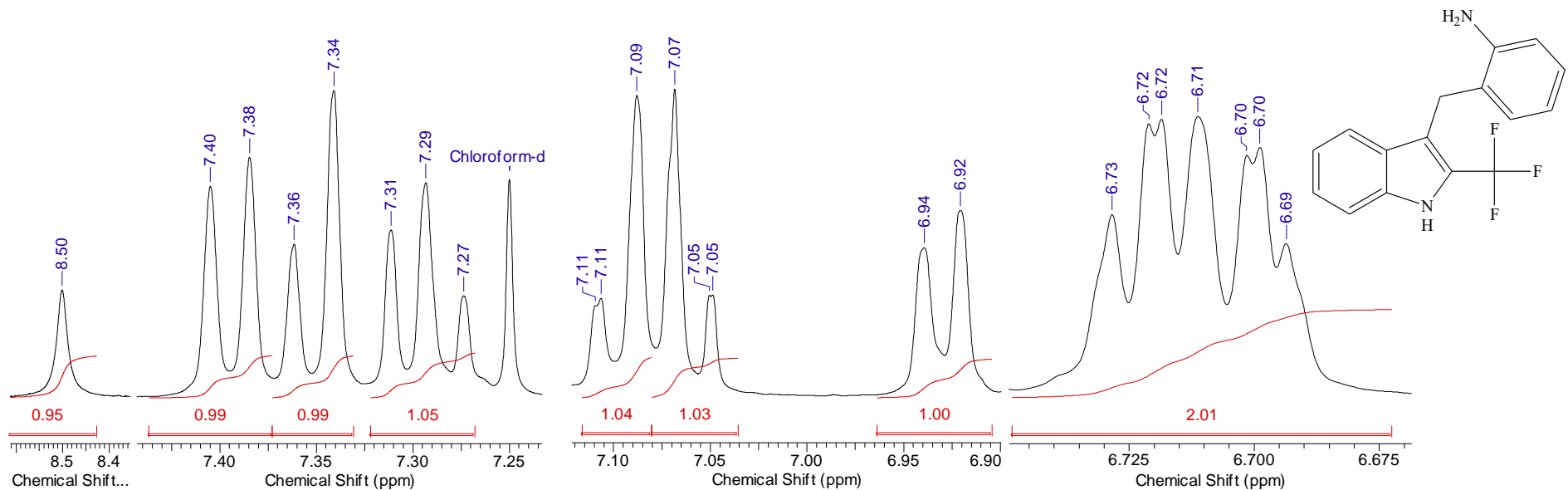


|                        |  |                       |                      |                        |        |                      |        |
|------------------------|--|-----------------------|----------------------|------------------------|--------|----------------------|--------|
| Acquisition Time (sec) | 0.6783   | Comment               | Imported from UXMNR. |                        | Date   | 29 Nov 2019 15:46:36 |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙兎BM-1804.C_002001r | Frequency (MHz)       | 100.61               | Nucleus                | 13C    |                      |        |
| Number of Transients   | 105  | Original Points Count | 16384                | Points Count           | 131072 | Pulse Sequence       | zgpg30 |
| Solvent                | CHLOROFORM-D                                     | Sweep Width (Hz)      | 24154.59             | Temperature (degree C) | 27.000 |                      |        |

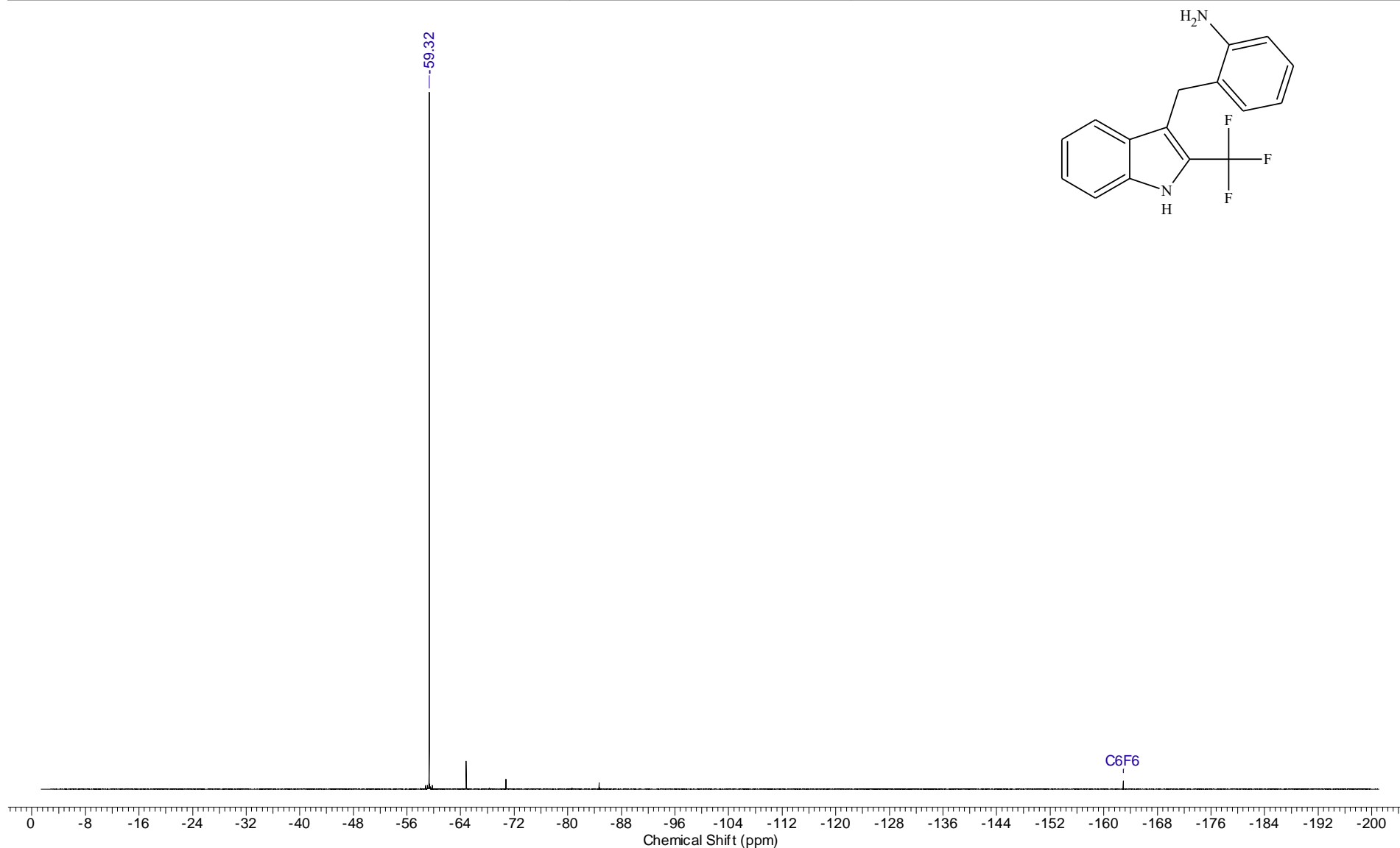


$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4k** (100.6 MHz,  $\text{CDCl}_3$ )



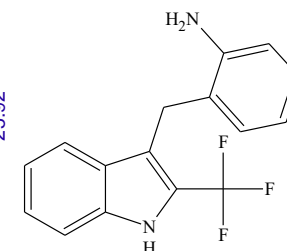
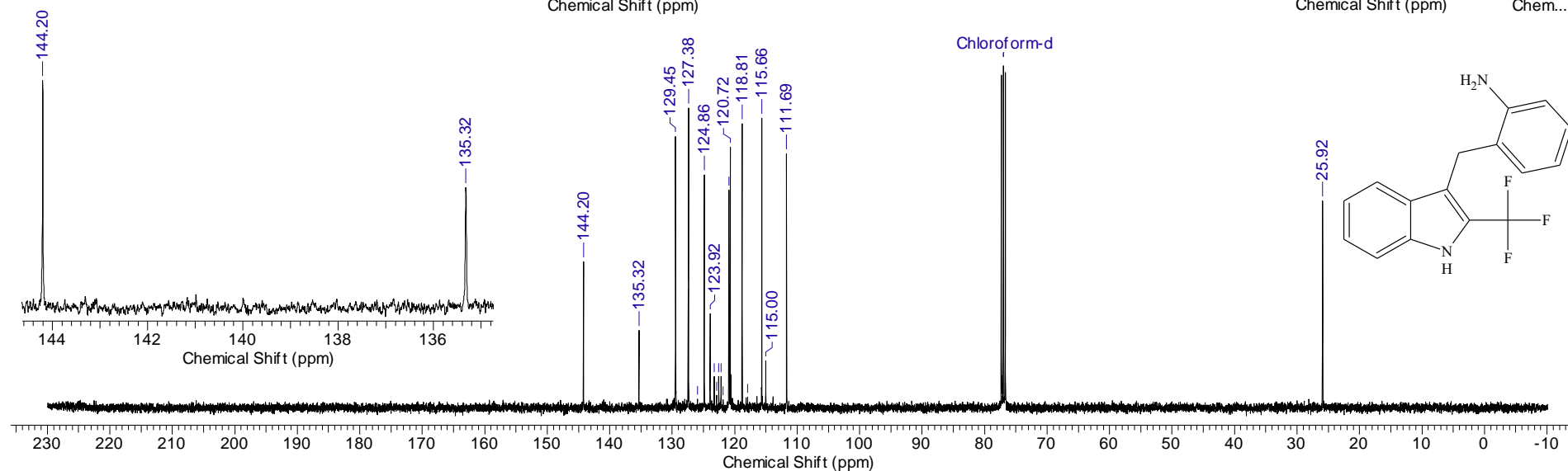
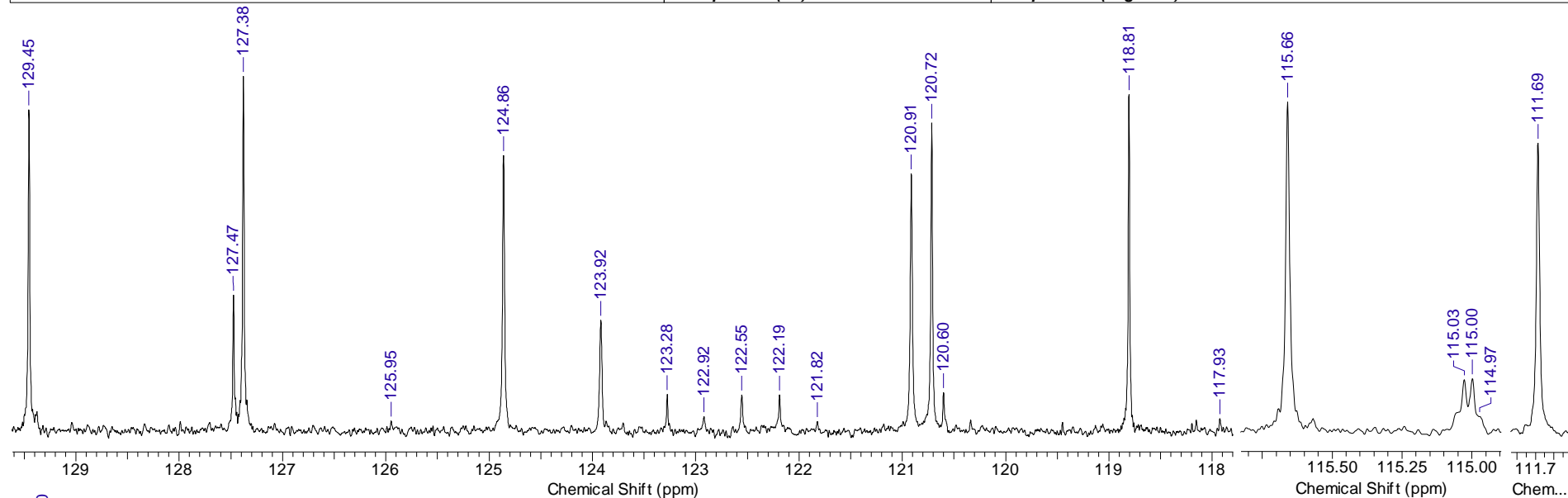
<sup>1</sup>H NMR spectrum of **4l** (400.1 MHz, CDCl<sub>3</sub>)

|                               |   |                              |                      |                               |             |                               |
|-------------------------------|---|------------------------------|----------------------|-------------------------------|-------------|-------------------------------|
| <b>Acquisition Time (sec)</b> | 1.7433                                  | <b>Comment</b>               | Imported from UXMNR. |                               | <b>Date</b> | 14 Jul 2020 20:54:04          |
| <b>File Name</b>              | C:\DOCS\BM\2020.07.14\BM-1893-2_005001r | <b>Frequency (MHz)</b>       | 376.50               | <b>Nucleus</b>                | 19F         |                               |
| <b>Number of Transients</b>   | 16                                      | <b>Original Points Count</b> | 131072               | <b>Points Count</b>           | 262144      | <b>Pulse Sequence</b> zgfglqn |
| <b>Solvent</b>                | CHLOROFORM-D                            | <b>Sweep Width (Hz)</b>      | 75187.97             | <b>Temperature (degree C)</b> | 27.000      |                               |

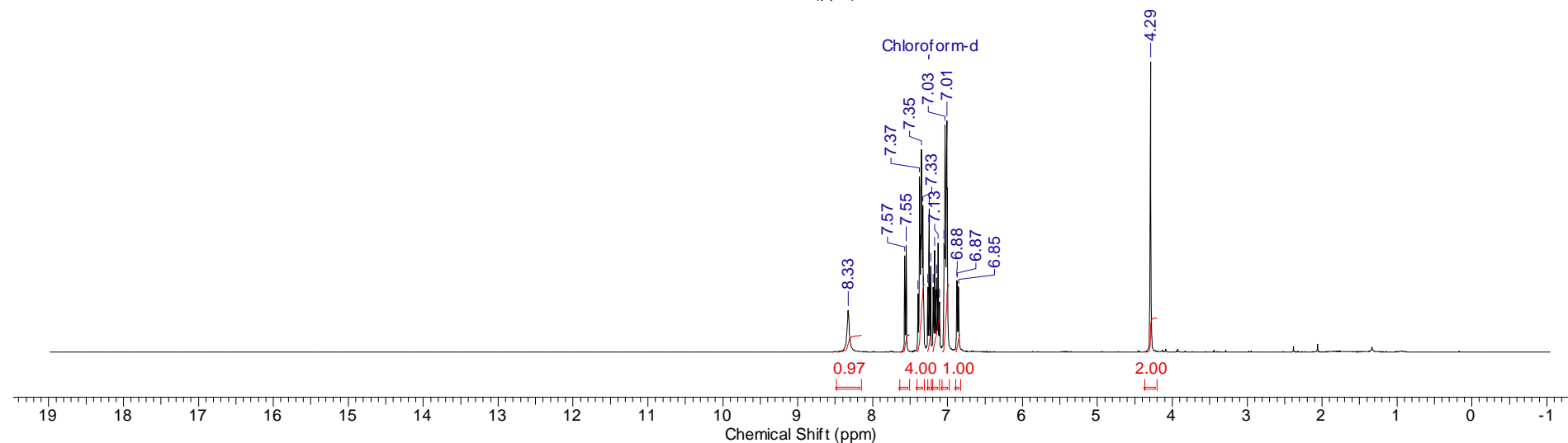
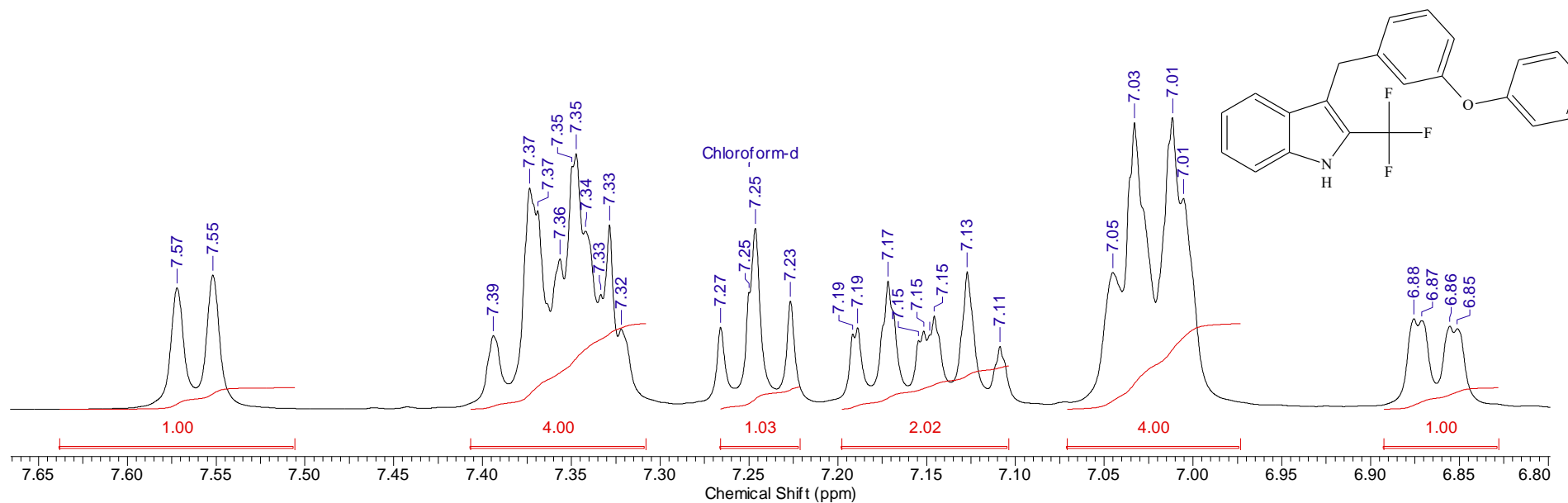
<sup>19</sup>F NMR spectrum of 4l (376.5 MHz, CDCl<sub>3</sub>)

S50

|                               |  |                              |                      |                               |             |                              |
|-------------------------------|--|------------------------------|----------------------|-------------------------------|-------------|------------------------------|
| <b>Acquisition Time (sec)</b> | 0.6783   | <b>Comment</b>               | Imported from UXNMR. |                               | <b>Date</b> | 14 Jul 2020 14:57:32         |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2020\07\樟 藤\BM-1893-2.C_002001r | <b>Frequency (MHz)</b>       | 100.61               | <b>Nucleus</b>                | 13C         |                              |
| <b>Number of Transients</b>   | 353  | <b>Original Points Count</b> | 16384                | <b>Points Count</b>           | 131072      | <b>Pulse Sequence</b> zgpg30 |
| <b>Solvent</b>                | CHLOROFORM-D                                       | <b>Sweep Width (Hz)</b>      | 24154.59             | <b>Temperature (degree C)</b> | 27.000      |                              |

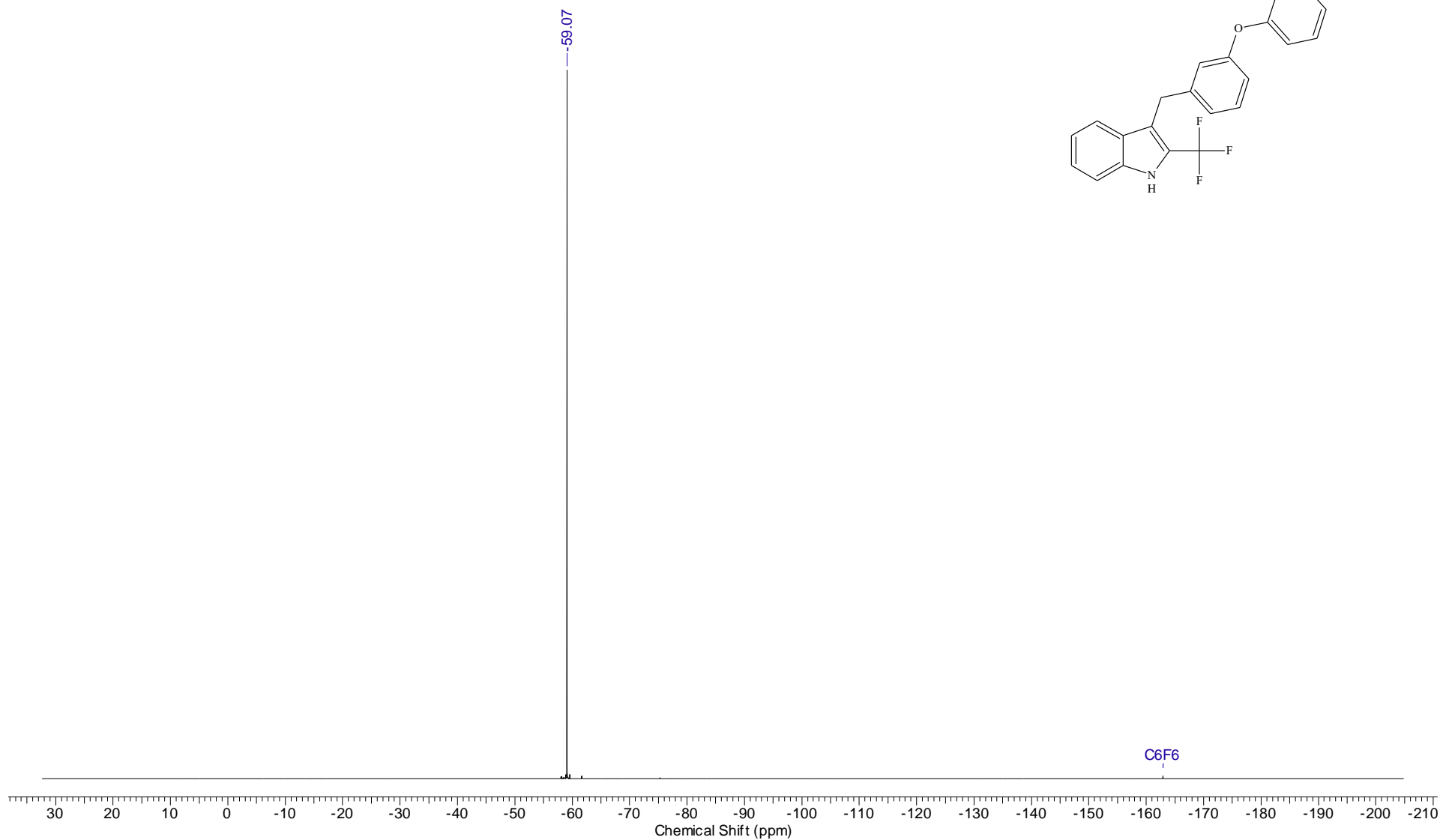
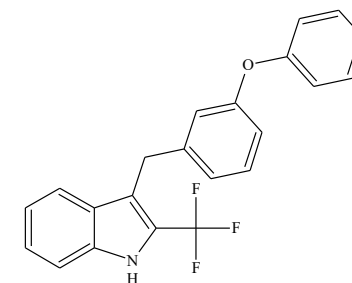
 $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4I** (100.6 MHz,  $\text{CDCl}_3$ )

|                        |  |                      |                      |                       |                 |                        |        |
|------------------------|--|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UXMNR. |                       | Date            | 26 Nov 2019 12:36:00   |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙鼎BM-1800.H_001001r |                      |                      |                       | Frequency (MHz) | 400.13                 |        |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768           | Points Count           | 131072 |
| Pulse Sequence         | zg30   | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 8012.82         | Temperature (degree C) | 27.000 |

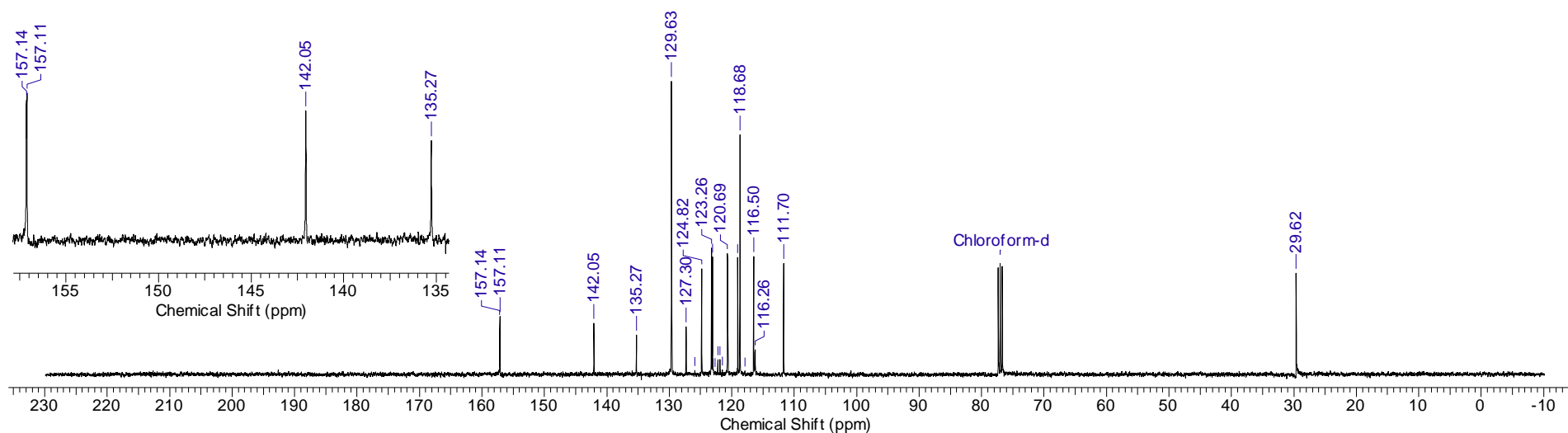
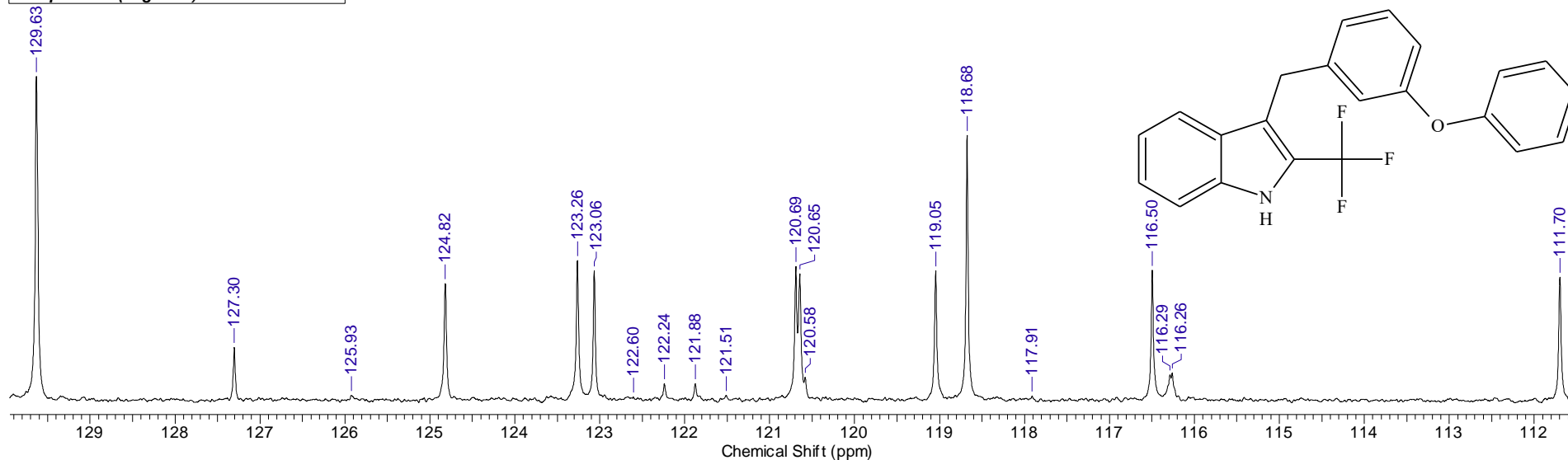
<sup>1</sup>H NMR spectrum of **4m** (400.1 MHz, CDCl<sub>3</sub>)

19 Jun 2020

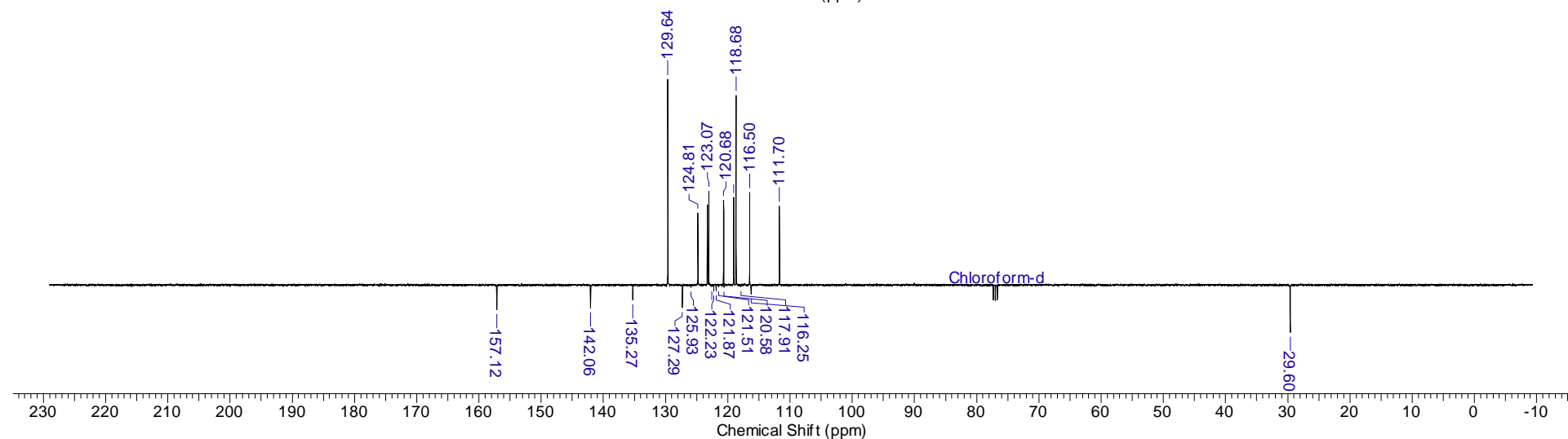
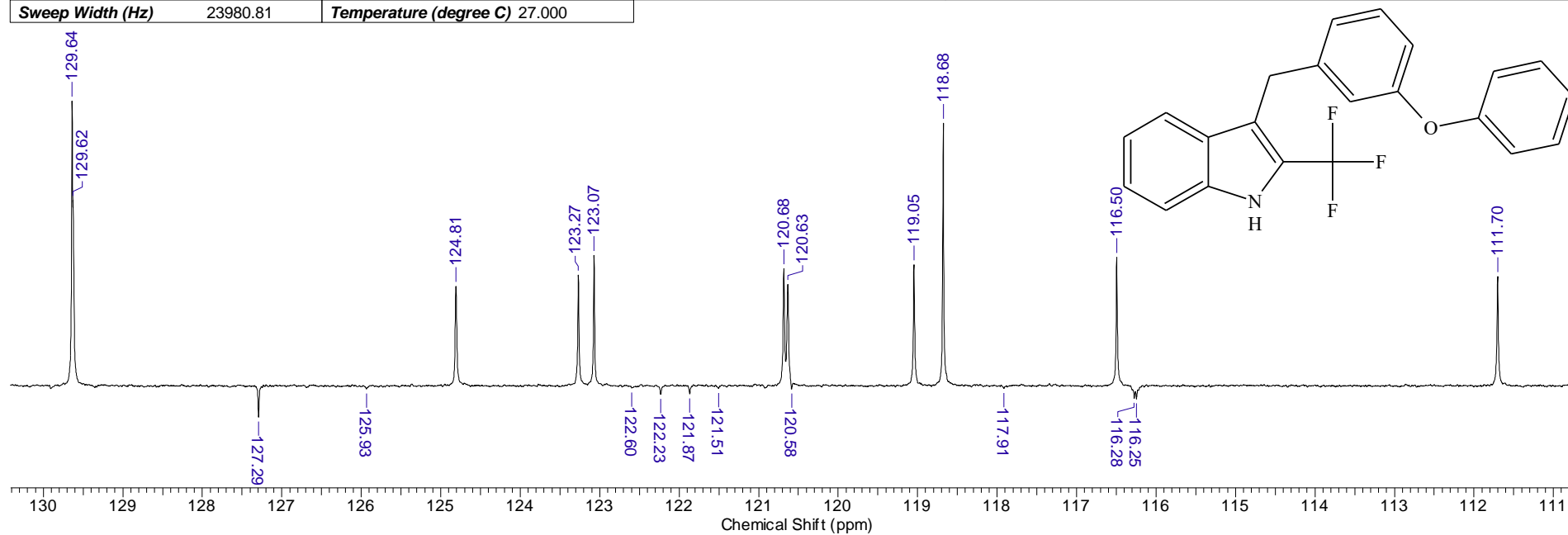
|                        |          |                        |             |                      |   |                             |
|------------------------|----------|------------------------|-------------|----------------------|---|-----------------------------|
| Acquisition Time (sec) | 1.0000   | Date                   | Nov 25 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.11.25\BM-1800_20191125_01\FLUORINE_01 |                             |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F         | Number of Transients | 16  | Original Points Count 89286 |
| Points Count           | 131072   | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D  |                             |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 20.000      |                      |   |                             |



|                        |  |                      |                      |                       |        |                  |                      |
|------------------------|--|----------------------|----------------------|-----------------------|--------|------------------|----------------------|
| Acquisition Time (sec) | 0.6783   | Comment              | Imported from UXNMR. |                       |        | Date             | 26 Nov 2019 09:38:08 |
| File Name              | C:\DOCS\OUTPUT_301\2019\11.脛 狙肱BM-1800.C\BM-1800.C_002000fid |                      |                      | Frequency (MHz)       | 100.62 |                  |                      |
| Nucleus                | 13C  | Number of Transients | 129                  | Original Points Count | 16384  | Points Count     | 131072               |
| Pulse Sequence         | zgpg30   | Solvent              | CHLOROFORM-D         |                       |        | Sweep Width (Hz) | 24154.59             |
| Temperature (degree C) | 27.000   |                      |                      |                       |        |                  |                      |

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4m** (100.6 MHz, CDCl<sub>3</sub>)

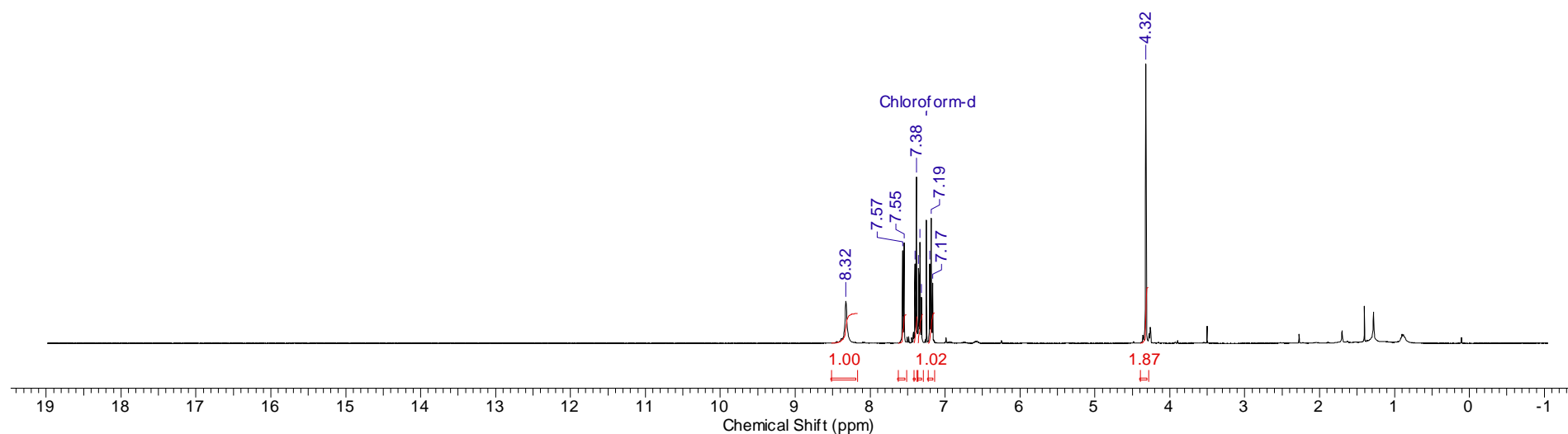
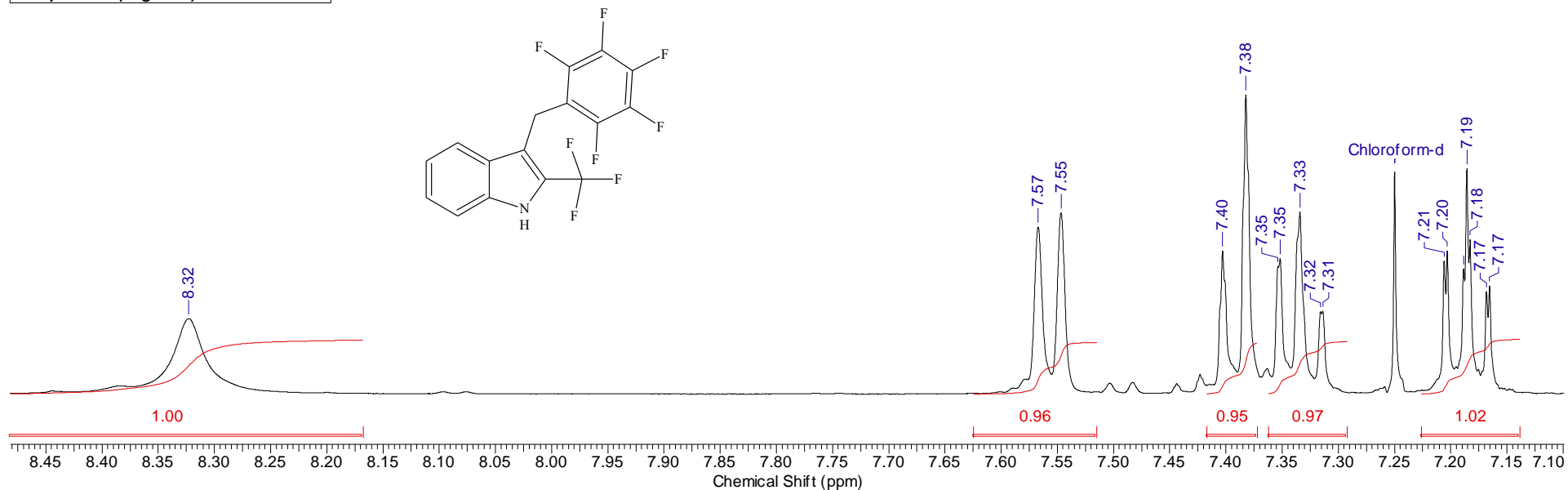
|                        |                                    |                        |                      |  |                |                      |                         |
|------------------------|------------------------------------|------------------------|----------------------|--|----------------|----------------------|-------------------------|
| Acquisition Time (sec) | 1.3664                             | Comment                | Imported from UXNMR. |  | Date           | 30 Nov 2019 23:12:52 |                         |
| File Name              | C:\DOCS\BM\BM-1800\BM-1800_004001r | Frequency (MHz)        | 100.61               |  | Nucleus        | 13C                  | Number of Transients 64 |
| Original Points Count  | 32768                              | Points Count           | 131072               |  | Pulse Sequence | jmod                 |                         |
| Sweep Width (Hz)       | 23980.81                           | Temperature (degree C) | 27.000               |  | Solvent        | CHLOROFORM-D         |                         |



$^{13}\text{C}\{^1\text{H}\}$  APT NMR spectrum of **4m** (100.6 MHz,  $\text{CDCl}_3$ )

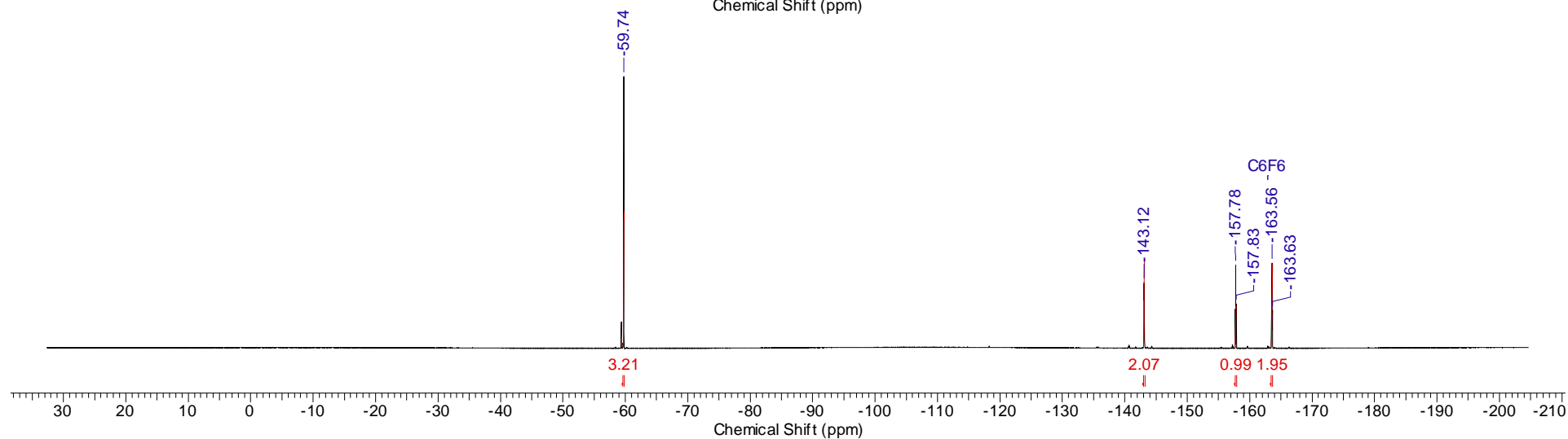
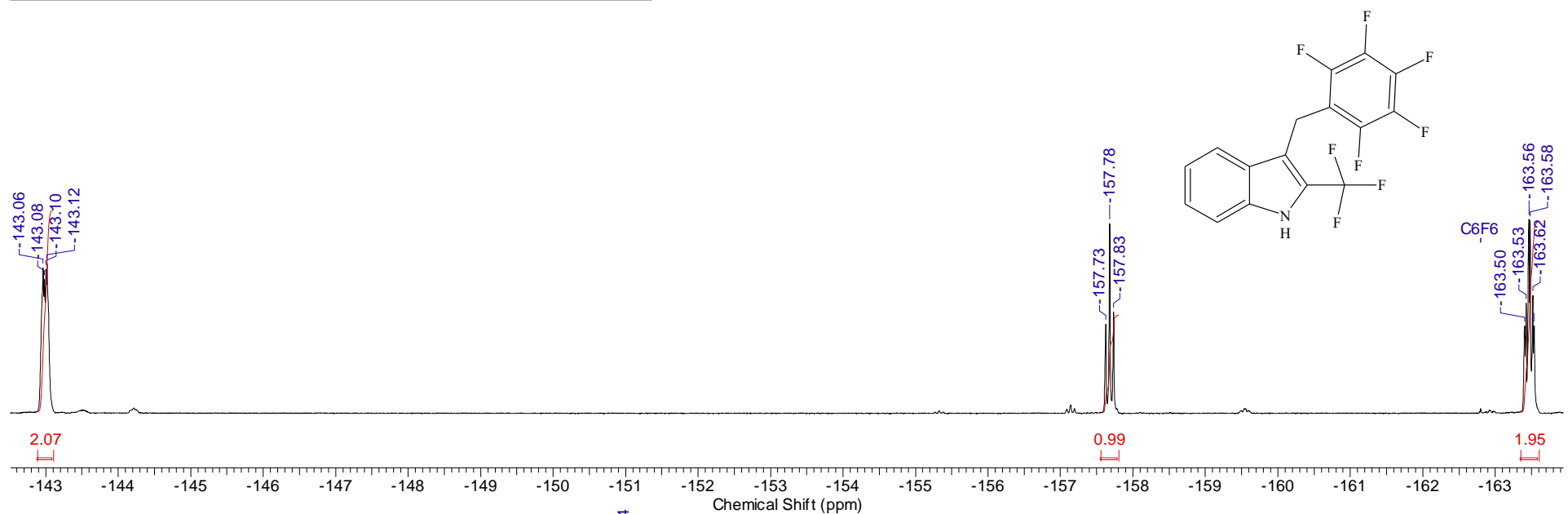
S55

|                               |  |                             |                      |                              |                      |
|-------------------------------|--|-----------------------------|----------------------|------------------------------|----------------------|
| <b>Acquisition Time (sec)</b> | 4.0894   | <b>Comment</b>              | Imported from UXNMR. | <b>Date</b>                  | 12 Dec 2019 12:19:10 |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2019\12\溴酚组黑BM-1824-1.H_001001r |                             |                      | <b>Frequency (MHz)</b>       | 400.13               |
| <b>Nucleus</b>                | <sup>1</sup> H                                     | <b>Number of Transients</b> | 4                    | <b>Original Points Count</b> | 32768                |
| <b>Pulse Sequence</b>         | zg30   | <b>Solvent</b>              | CHLOROFORM-D         | <b>Points Count</b>          | 131072               |
| <b>Temperature (degree C)</b> | 27.000   |                             |                      | <b>Sweep Width (Hz)</b>      | 8012.82              |

<sup>1</sup>H NMR spectrum of **4n** (400.1 MHz, CDCl<sub>3</sub>).

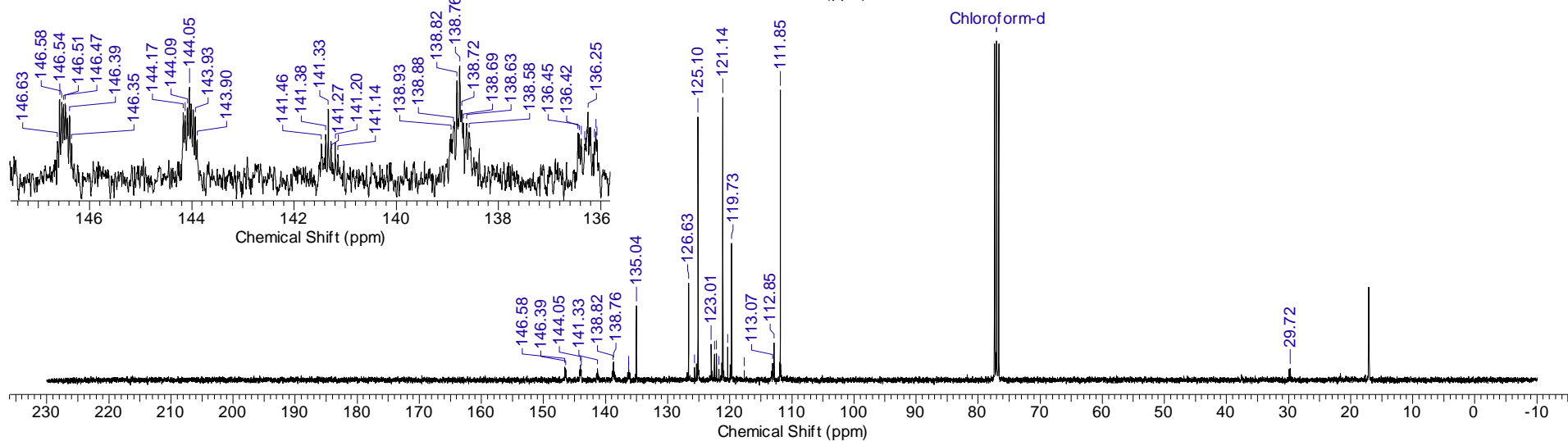
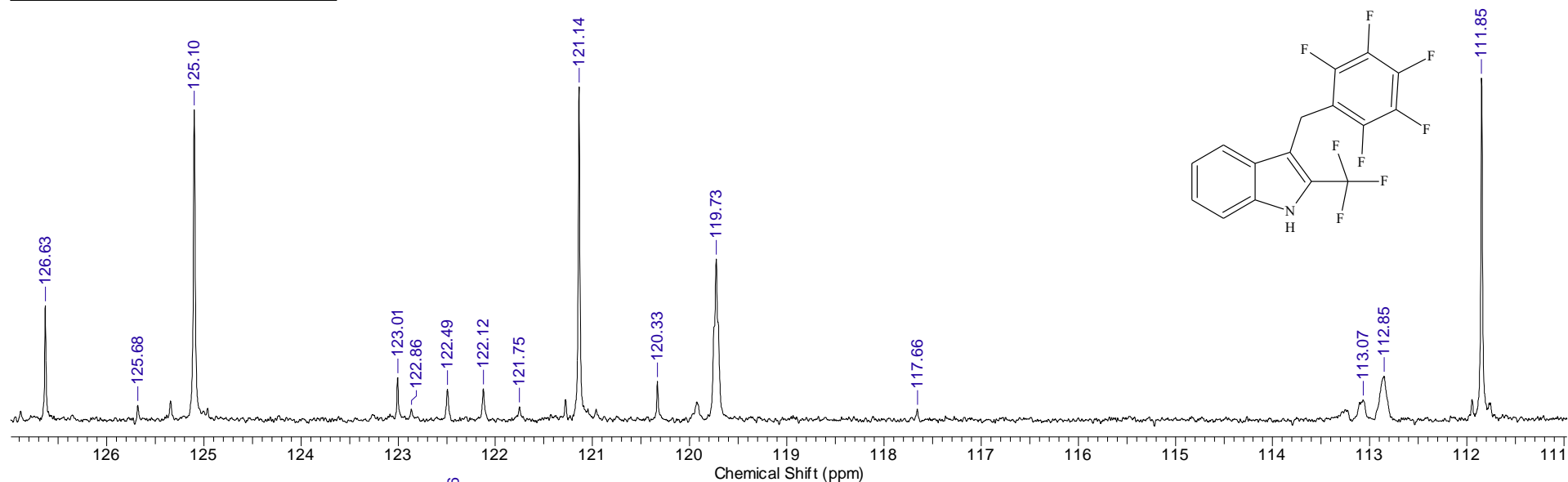


|                        |          |                        |             |                      |   |                             |
|------------------------|----------|------------------------|-------------|----------------------|---|-----------------------------|
| Acquisition Time (sec) | 0.7340   | Date                   | Dec 13 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.12.13\BM-1824-1_20191213_01\FLUORINE_01 |                             |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F         | Number of Transients | 1   | Original Points Count 65536 |
| Points Count           | 65536    | Pulse Sequence         | s2pul       | Solvent              | CHLOROFORM-D  |                             |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 30.000      |                      |   |                             |

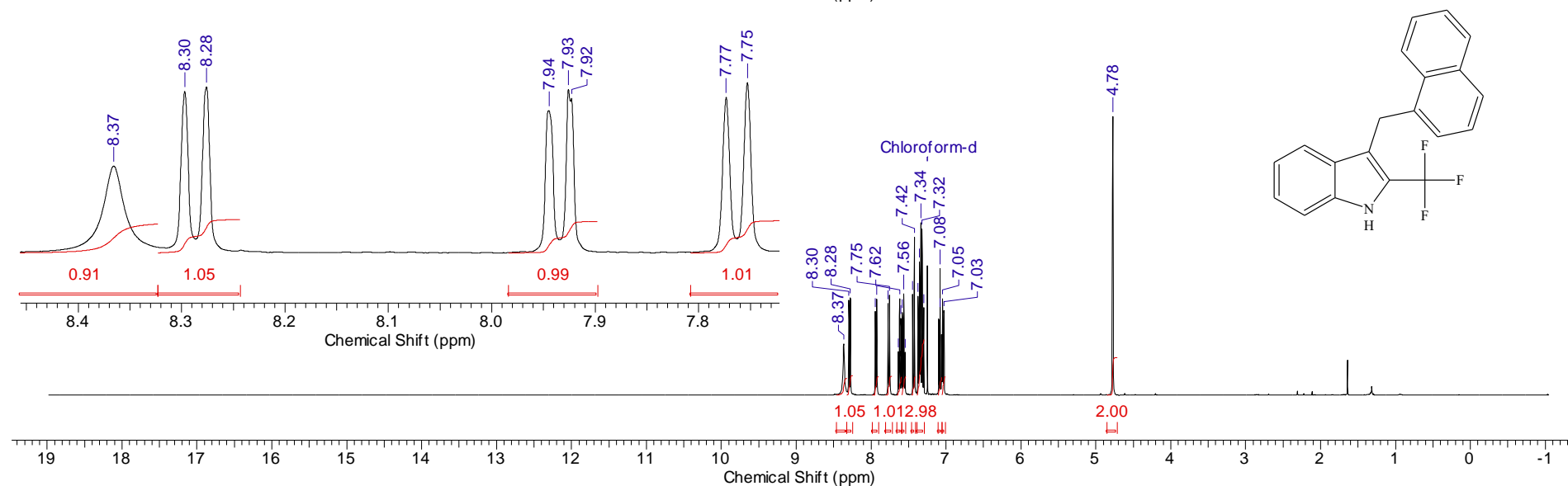
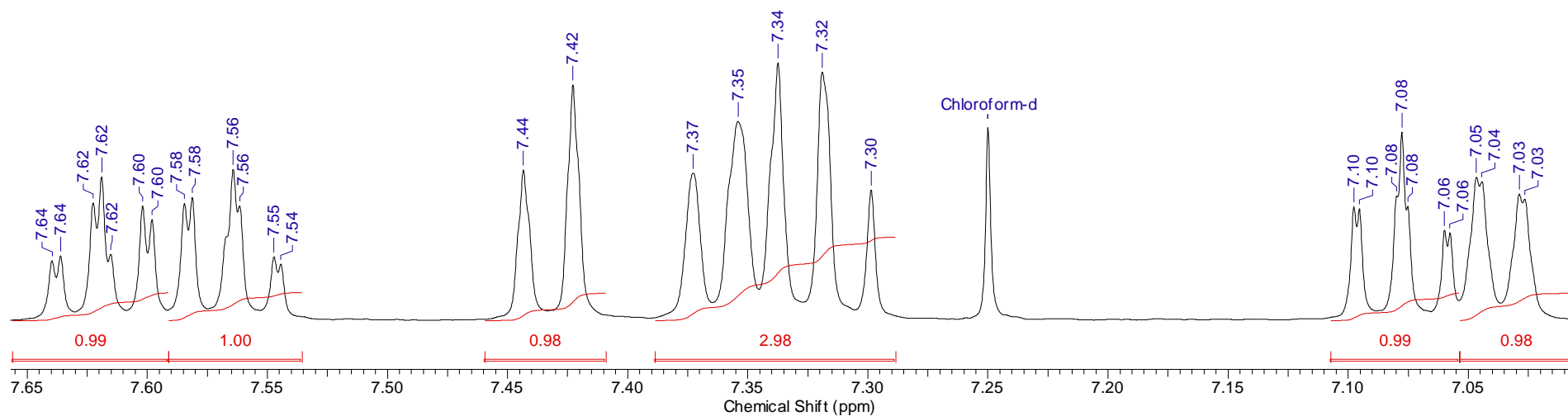


$^{19}\text{F}$  NMR spectrum of **4n** (376.5 MHz,  $\text{CDCl}_3$ )

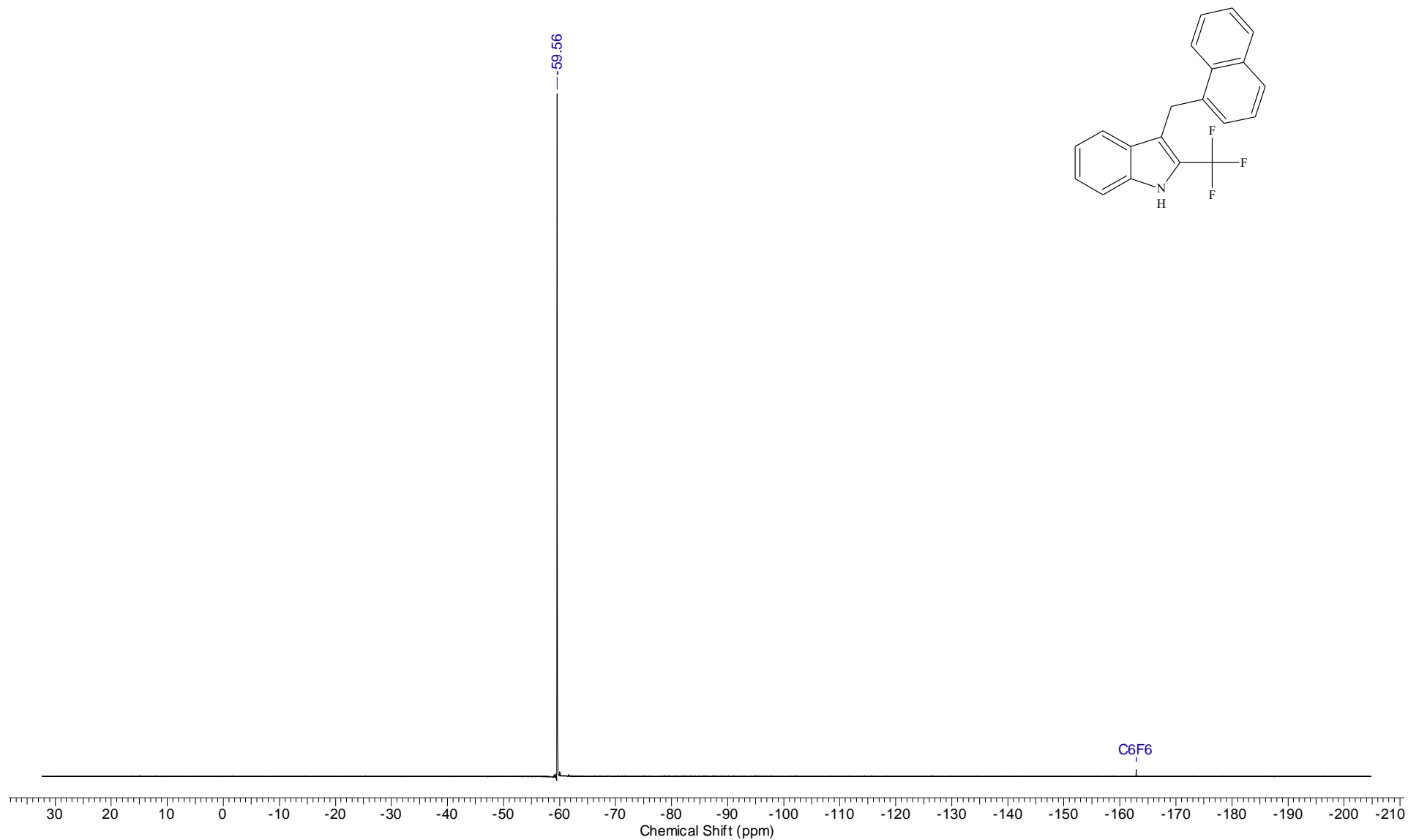
|                        |  |                              |              |                       |                  |                      |        |
|------------------------|--|------------------------------|--------------|-----------------------|------------------|----------------------|--------|
| Acquisition Time (sec) | 0.6783   | Comment Imported from UXNMR. |              |                       | Date             | 12 Dec 2019 12:43:54 |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\12.溴吡喹啉BM-1824-1.C_002001r |                              |              |                       | Frequency (MHz)  | 100.61               |        |
| Nucleus                | 13C  | Number of Transients         | 626          | Original Points Count | 16384            | Points Count         | 131072 |
| Pulse Sequence         | zgpg30   | Solvent                      | CHLOROFORM-D |                       | Sweep Width (Hz) | 24154.59             |        |
| Temperature (degree C) | 27.000   |                              |              |                       |                  |                      |        |

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4n** (100.6 MHz, CDCl<sub>3</sub>)

|                               |  |                             |                      |                              |                      |
|-------------------------------|--|-----------------------------|----------------------|------------------------------|----------------------|
| <b>Acquisition Time (sec)</b> | 4.0894   | <b>Comment</b>              | Imported from UXNMR. | <b>Date</b>                  | 02 Dec 2019 15:51:50 |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2019\12.溴脛狙黑BM-1802-1.H_001001r | <b>Frequency (MHz)</b>      | 400.13               | <b>Points Count</b>          | 131072               |
| <b>Nucleus</b>                | <sup>1</sup> H                                     | <b>Number of Transients</b> | 7                    | <b>Original Points Count</b> | 32768                |
| <b>Pulse Sequence</b>         | zg30   | <b>Solvent</b>              | CHLOROFORM-D         | <b>Sweep Width (Hz)</b>      | 8012.82              |
| <b>Temperature (degree C)</b> | 27.000   |                             |                      |                              |                      |

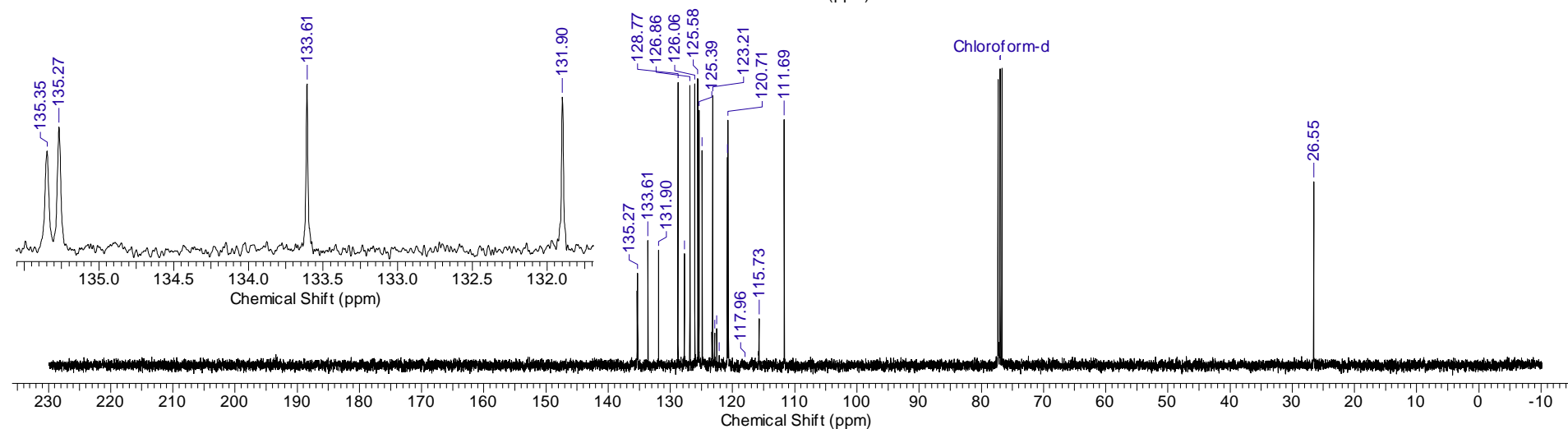
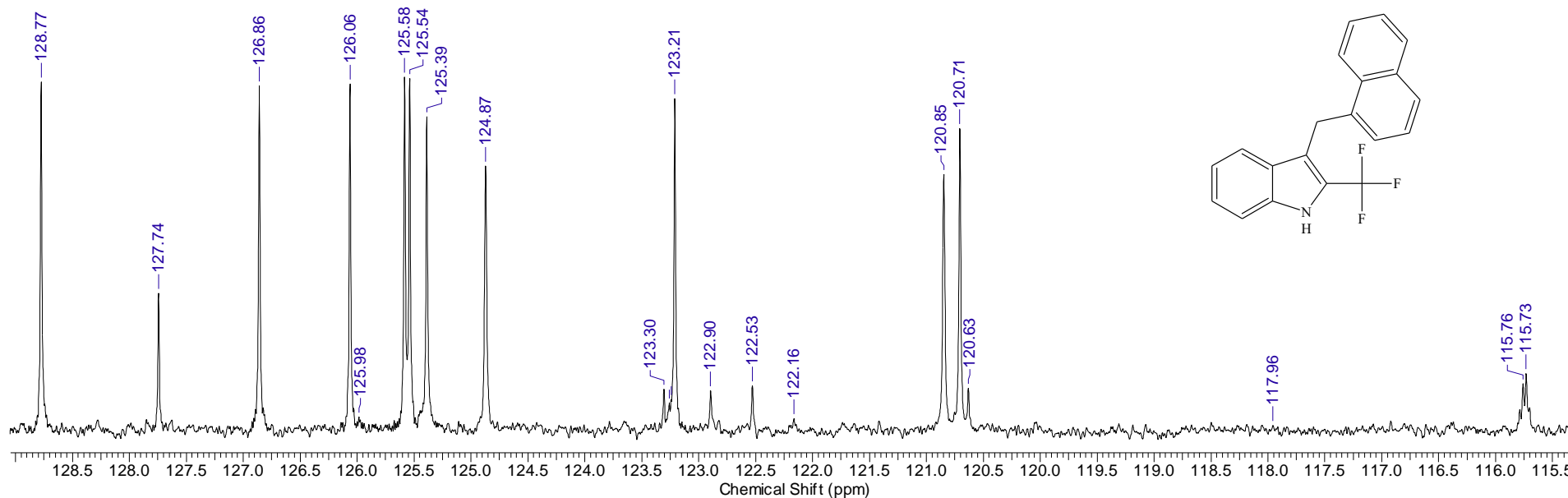
<sup>1</sup>H NMR spectrum of **4o** (400.1 MHz, CDCl<sub>3</sub>)

|                        |          |                        |            |                      |   |                              |
|------------------------|----------|------------------------|------------|----------------------|---|------------------------------|
| Acquisition Time (sec) | 2.0000   | Date                   | Dec 2 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.12.02\BM-1802-1_20191202_01\FLUORINE_01 |                              |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F        | Number of Transients | 16  | Original Points Count 178571 |
| Points Count           | 262144   | Pulse Sequence         | s2pul      | Solvent              | CHLOROFORM-D  |                              |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 22.000     |                      |   |                              |

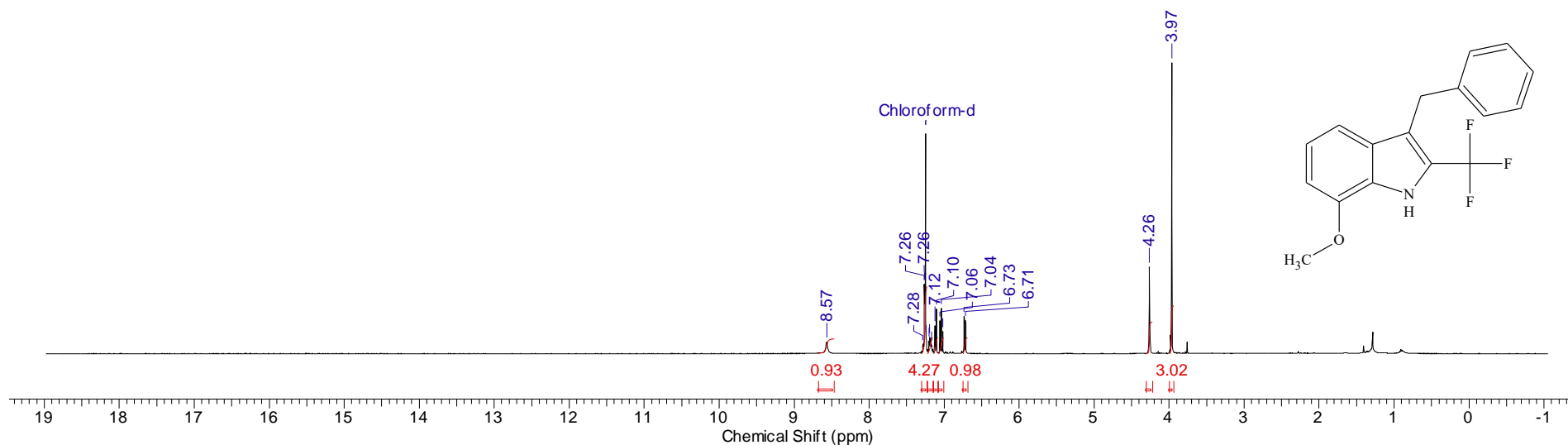
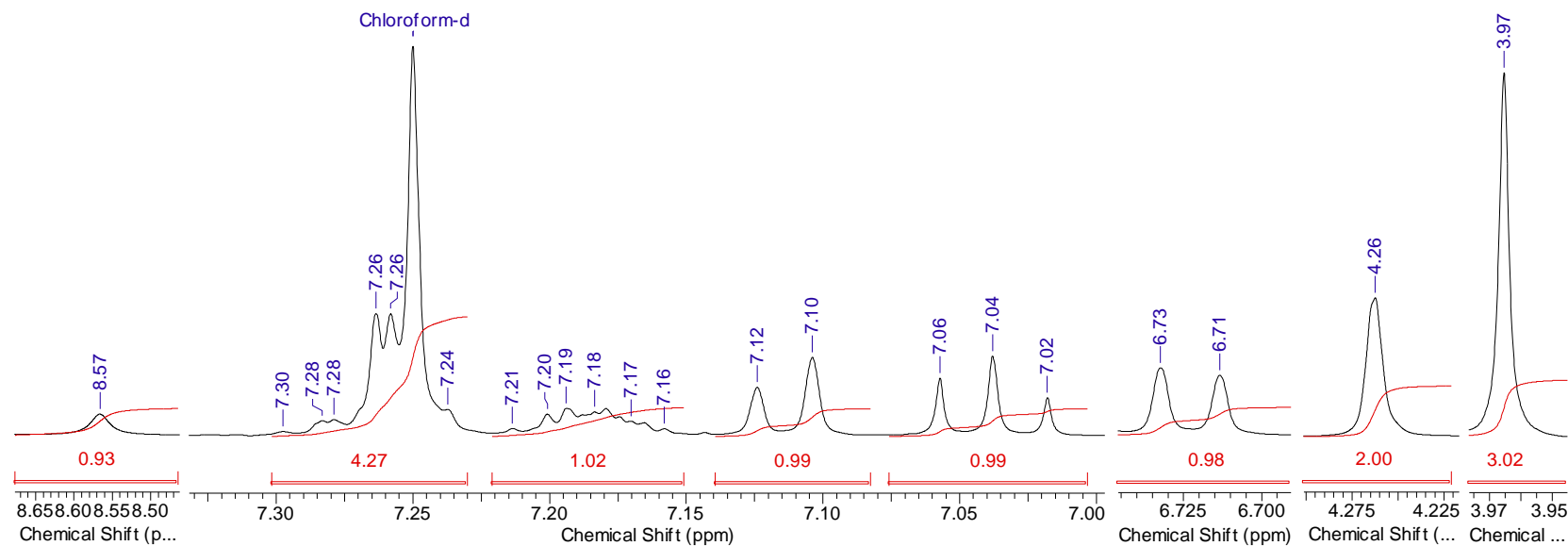
 $^{19}\text{F}$  NMR spectrum of **4o** (376.5 MHz,  $\text{CDCl}_3$ )

S60

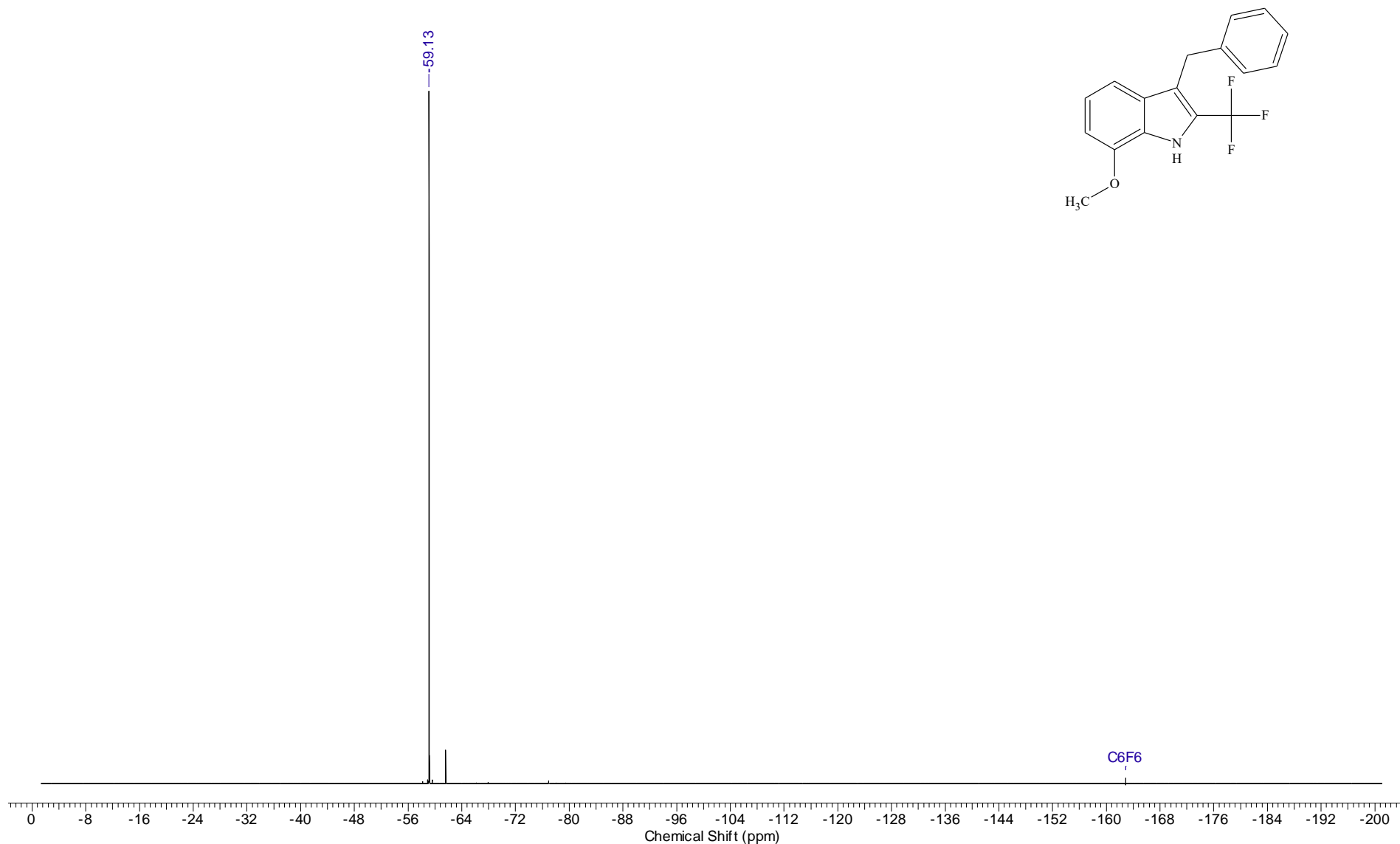
|                        |  |                      |                      |                       |                  |                      |        |
|------------------------|--|----------------------|----------------------|-----------------------|------------------|----------------------|--------|
| Acquisition Time (sec) | 0.6783   | Comment              | Imported from UXNMR. |                       | Date             | 02 Dec 2019 15:57:02 |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\12.溴脛狙黑BM-1802-1.C_002001r |                      |                      |                       | Frequency (MHz)  | 100.61               |        |
| Nucleus                | 13C  | Number of Transients | 122                  | Original Points Count | 16384            | Points Count         | 131072 |
| Pulse Sequence         | zgpg30   | Solvent              | CHLOROFORM-D         |                       | Sweep Width (Hz) | 24154.59             |        |
| Temperature (degree C) | 27.000   |                      |                      |                       |                  |                      |        |

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **4o** (100.6 MHz, CDCl<sub>3</sub>)

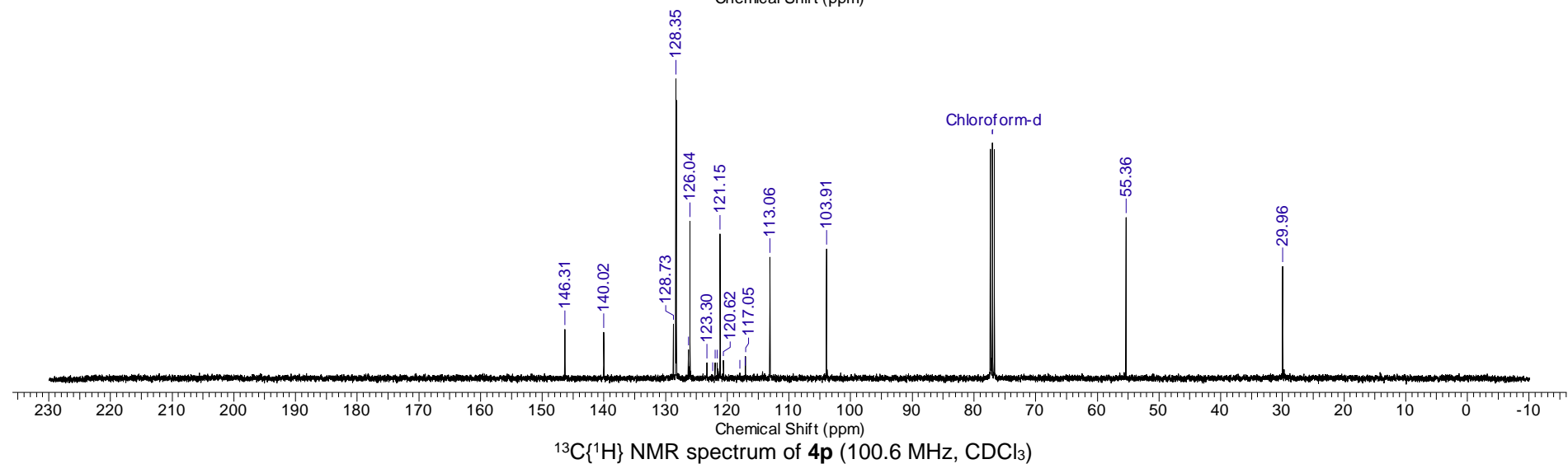
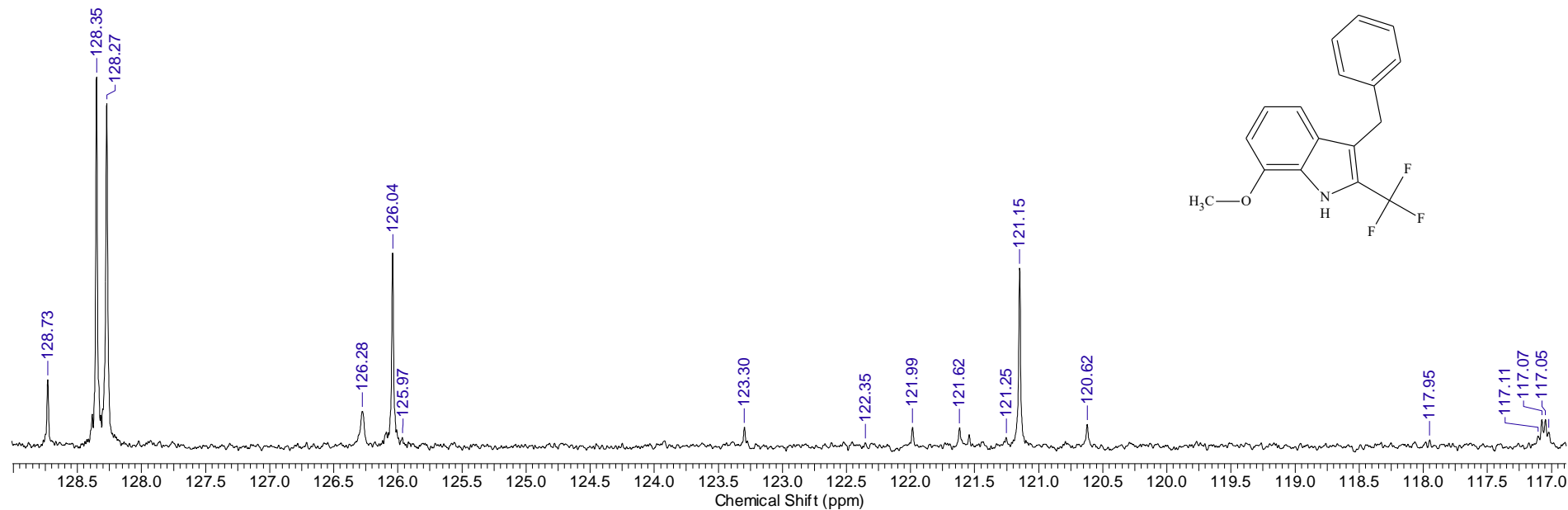
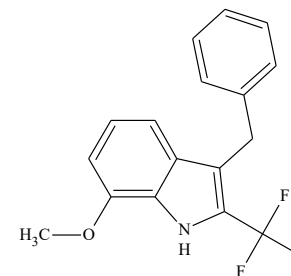
|                               |  |                               |                      |                       |             |                             |              |
|-------------------------------|--|-------------------------------|----------------------|-----------------------|-------------|-----------------------------|--------------|
| <b>Acquisition Time (sec)</b> | 4.0894                                 | <b>Comment</b>                | Imported from UXNMR. |                       | <b>Date</b> | 11 Jul 2020 21:52:54        |              |
| <b>File Name</b>              | C:\BM_DATA\DOCS\200711\BM-1896_001001r | <b>Frequency (MHz)</b>        | 400.13               | <b>Nucleus</b>        | 1H          | <b>Number of Transients</b> | 8            |
| <b>Original Points Count</b>  | 32768                                  | <b>Points Count</b>           | 131072               | <b>Pulse Sequence</b> | zg30        | <b>Solvent</b>              | CHLOROFORM-D |
| <b>Sweep Width (Hz)</b>       | 8012.82                                | <b>Temperature (degree C)</b> | 27.000               |                       |             |                             |              |

<sup>1</sup>H NMR spectrum of **4p** (400.1 MHz, CDCl<sub>3</sub>)

|                               |  |                              |                      |                               |             |                              |
|-------------------------------|--|------------------------------|----------------------|-------------------------------|-------------|------------------------------|
| <b>Acquisition Time (sec)</b> | 1.7433                                 | <b>Comment</b>               | Imported from UXMNR. |                               | <b>Date</b> | 11 Jul 2020 21:54:32         |
| <b>File Name</b>              | C:\BM_DATA\DOCS\200711\BM-1896_005001r | <b>Frequency (MHz)</b>       | 376.50               | <b>Nucleus</b>                | 19F         |                              |
| <b>Number of Transients</b>   | 16                                     | <b>Original Points Count</b> | 131072               | <b>Points Count</b>           | 262144      | <b>Pulse Sequence</b> zgfgqn |
| <b>Solvent</b>                | CHLOROFORM-D                           | <b>Sweep Width (Hz)</b>      | 75187.97             | <b>Temperature (degree C)</b> | 27.000      |                              |

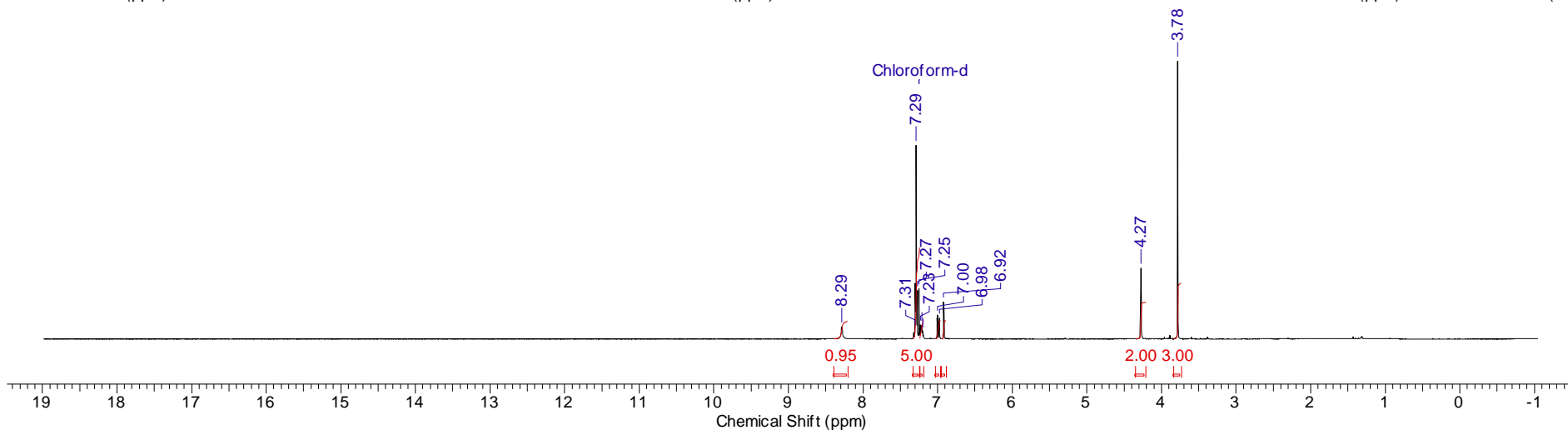
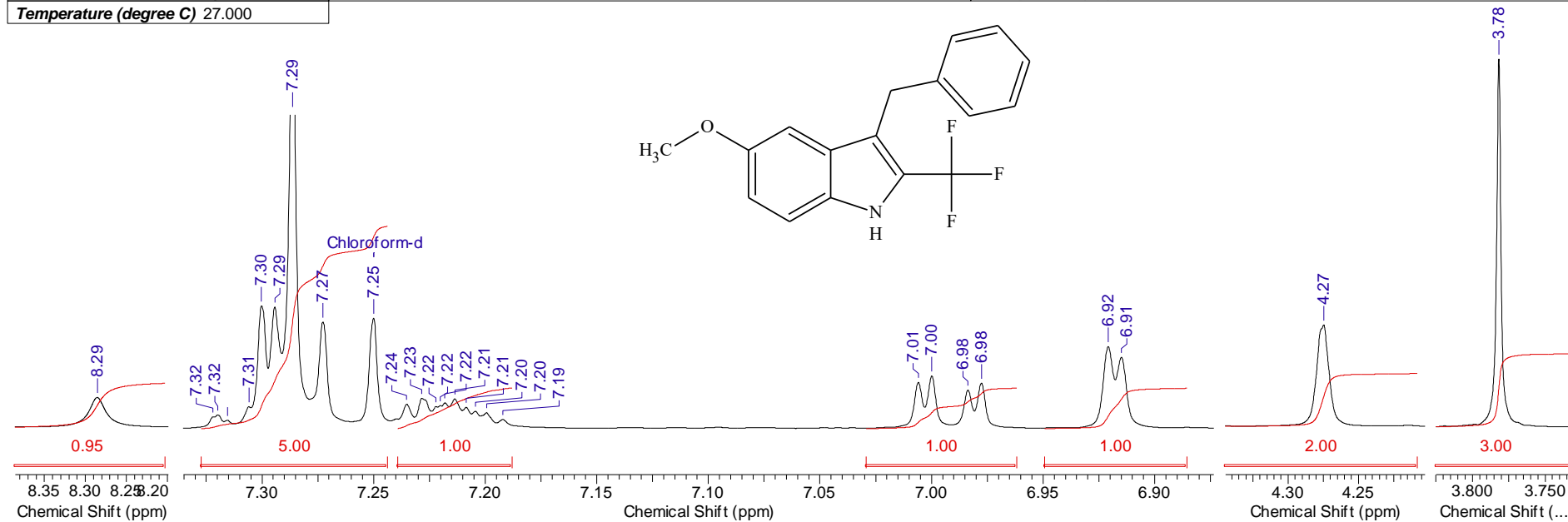


|                               |  |                              |                      |                               |             |                      |
|-------------------------------|--|------------------------------|----------------------|-------------------------------|-------------|----------------------|
| <b>Acquisition Time (sec)</b> | 0.6783   | <b>Comment</b>               | Imported from UXNMR. |                               | <b>Date</b> | 10 Jul 2020 15:50:00 |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2020\07\樟 藤\BM-1896.C_002001r | <b>Frequency (MHz)</b>       | 100.61               | <b>Nucleus</b>                | 13C         |                      |
| <b>Number of Transients</b>   | 266  | <b>Original Points Count</b> | 16384                | <b>Points Count</b>           | 131072      |                      |
| <b>Solvent</b>                | CHLOROFORM-D                                     | <b>Sweep Width (Hz)</b>      | 24154.59             | <b>Pulse Sequence</b>         | zgpg30      |                      |
|                               |  |                              |                      | <b>Temperature (degree C)</b> | 27.000      |                      |

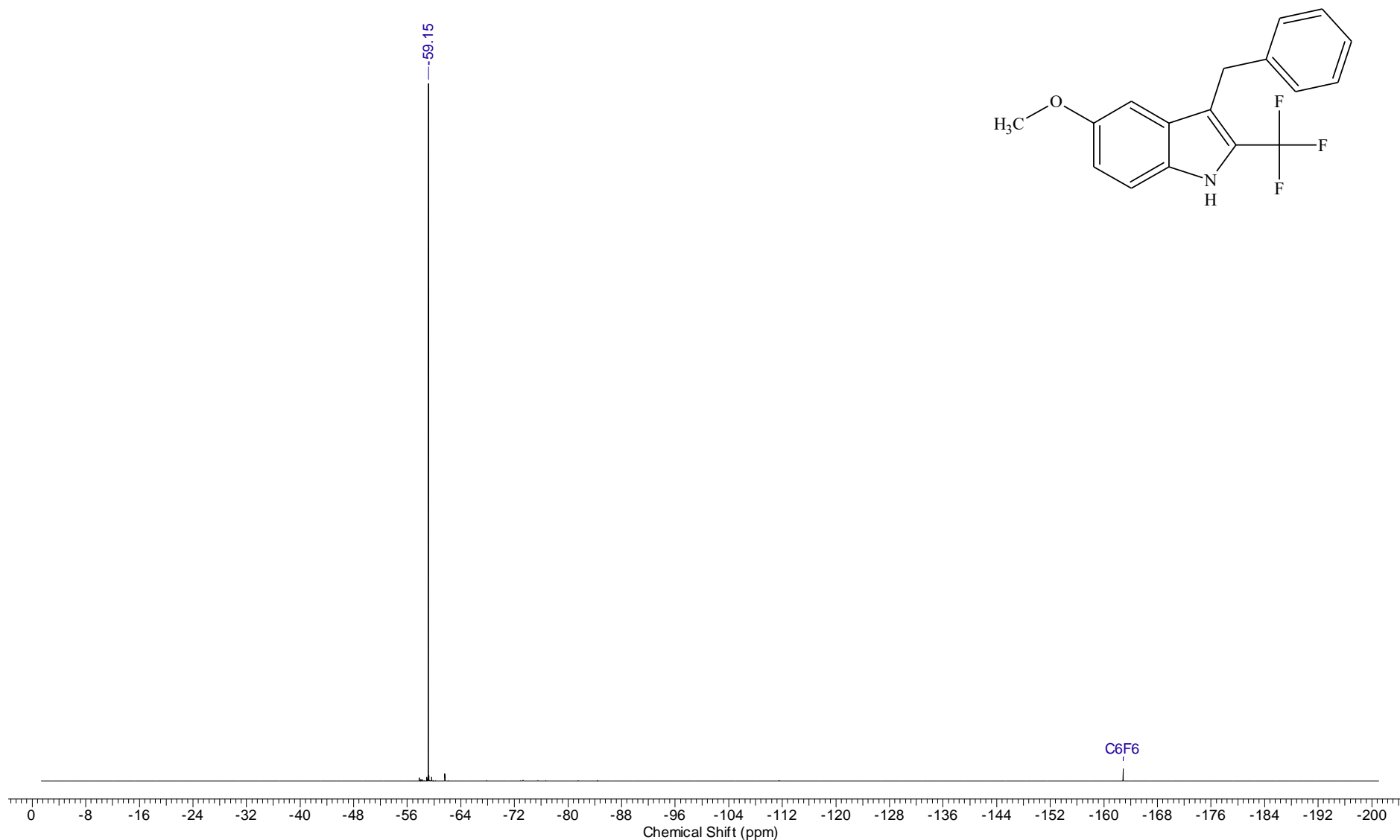




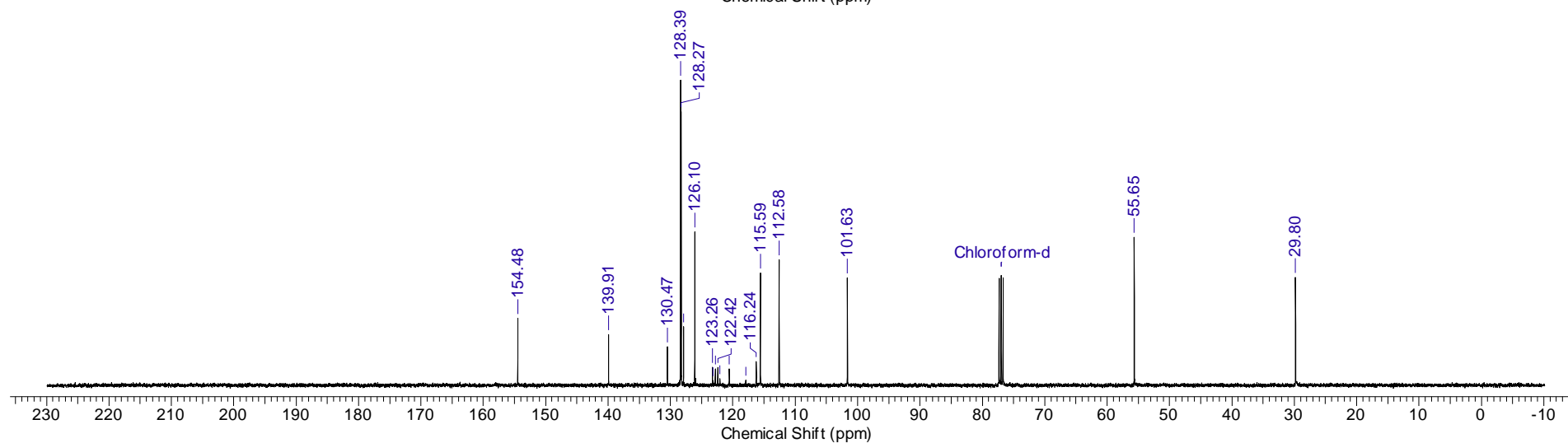
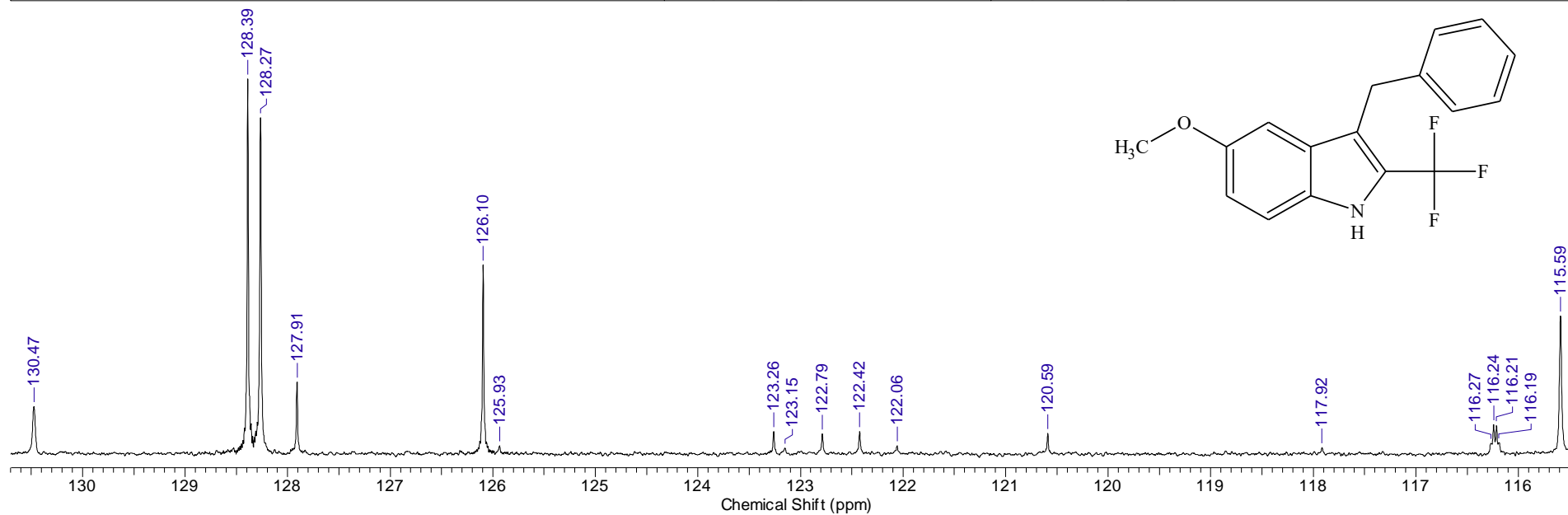
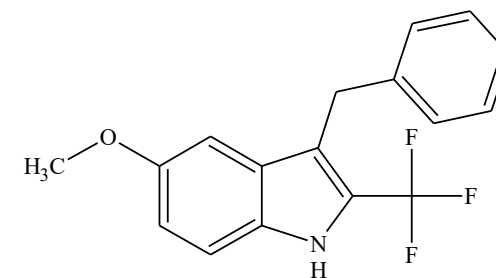
|                        |  |                      |                      |                       |                  |                      |        |
|------------------------|--|----------------------|----------------------|-----------------------|------------------|----------------------|--------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UXMNR. |                       | Date             | 10 Apr 2021 13:30:22 |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\04.因孢藤\BM-2130.H_001001r |                      |                      |                       | Frequency (MHz)  | 400.13               |        |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768            | Points Count         | 131072 |
| Pulse Sequence         | zg30   | Solvent              | CHLOROFORM-D         |                       | Sweep Width (Hz) | 8012.82              |        |
| Temperature (degree C) | 27.000   |                      |                      |                       |                  |                      |        |

<sup>1</sup>H NMR spectrum of **4q** (400.1 MHz, CDCl<sub>3</sub>)

|                        |  |                      |                      |                       |          |                        |                      |
|------------------------|--|----------------------|----------------------|-----------------------|----------|------------------------|----------------------|
| Acquisition Time (sec) | 1.7433   | Comment              | Imported from UXNMR. |                       |          | Date                   | 10 Apr 2021 13:44:20 |
| File Name              | C:\DOCS\OUTPUT_301\2021\04\因孢藤\BM-2130.F_005001r |                      |                      |                       |          | Frequency (MHz)        | 376.50               |
| Nucleus                | 19F  | Number of Transients | 16                   | Original Points Count | 131072   | Points Count           | 262144               |
| Pulse Sequence         | zgfgqn   | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 75187.97 | Temperature (degree C) | 27.000               |

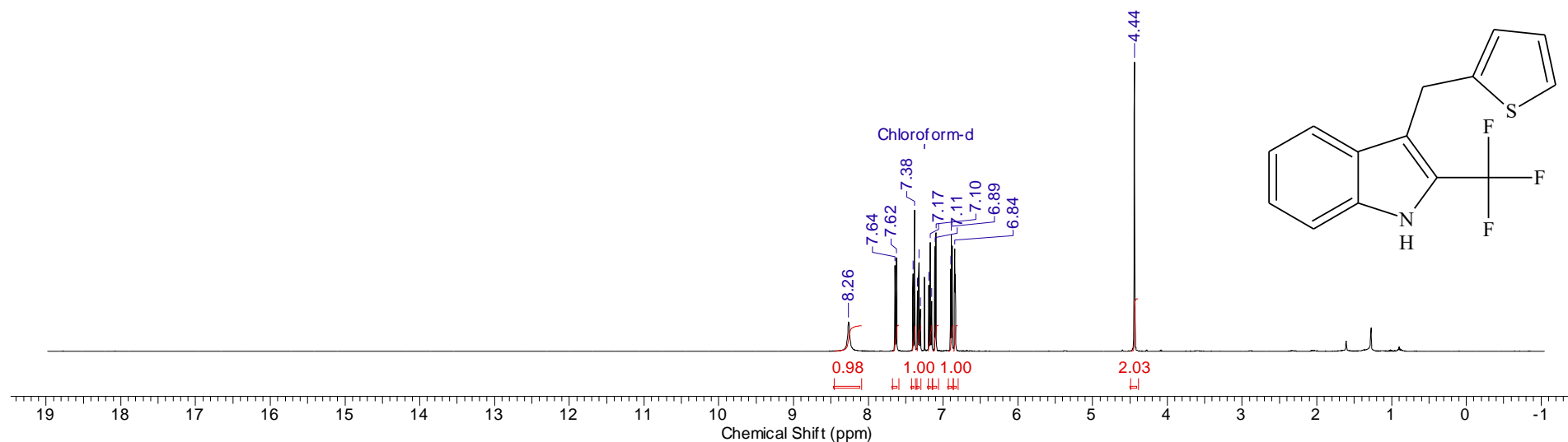
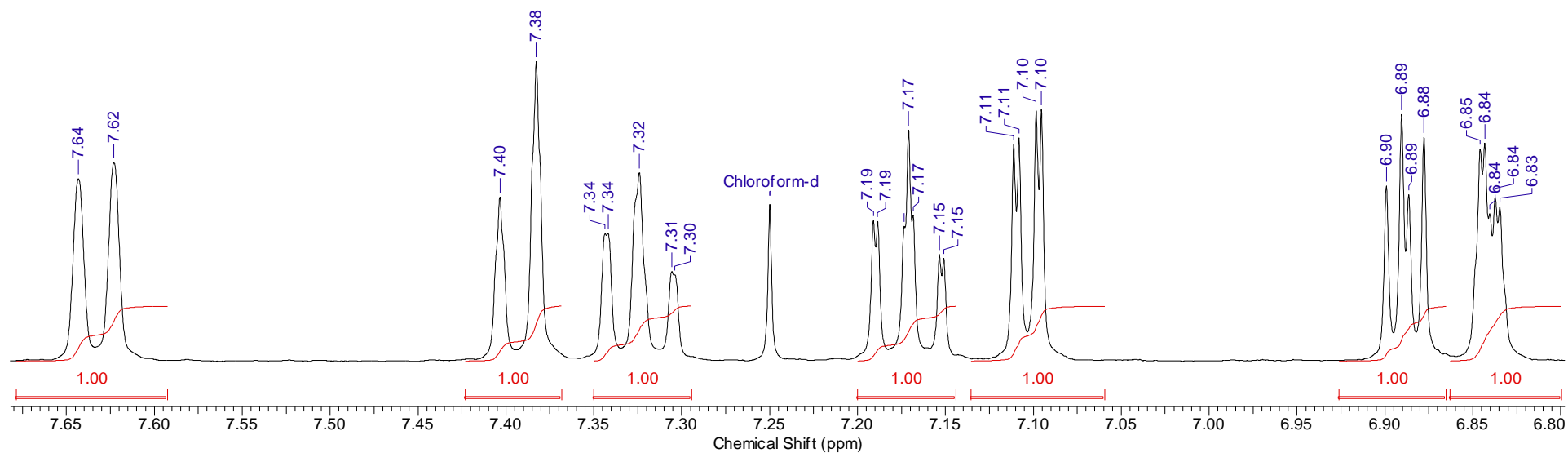


|                        |  |                       |                      |  |                        |                      |  |
|------------------------|--|-----------------------|----------------------|--|------------------------|----------------------|--|
| Acquisition Time (sec) | 0.6783   | Comment               | Imported from UxNMR. |  | Date                   | 10 Apr 2021 13:40:10 |  |
| File Name              | C:\DOCS\OUTPUT_301\2021\04.因孢腺\BM-2130.C_002001r | Frequency (MHz)       | 100.61               |  | Nucleus                | 13C                  |  |
| Number of Transients   | 201  | Original Points Count | 16384                |  | Pulse Sequence         | zgpg30               |  |
| Solvent                | CHLOROFORM-D                                     | Sweep Width (Hz)      | 24154.59             |  | Temperature (degree C) | 27.000               |  |

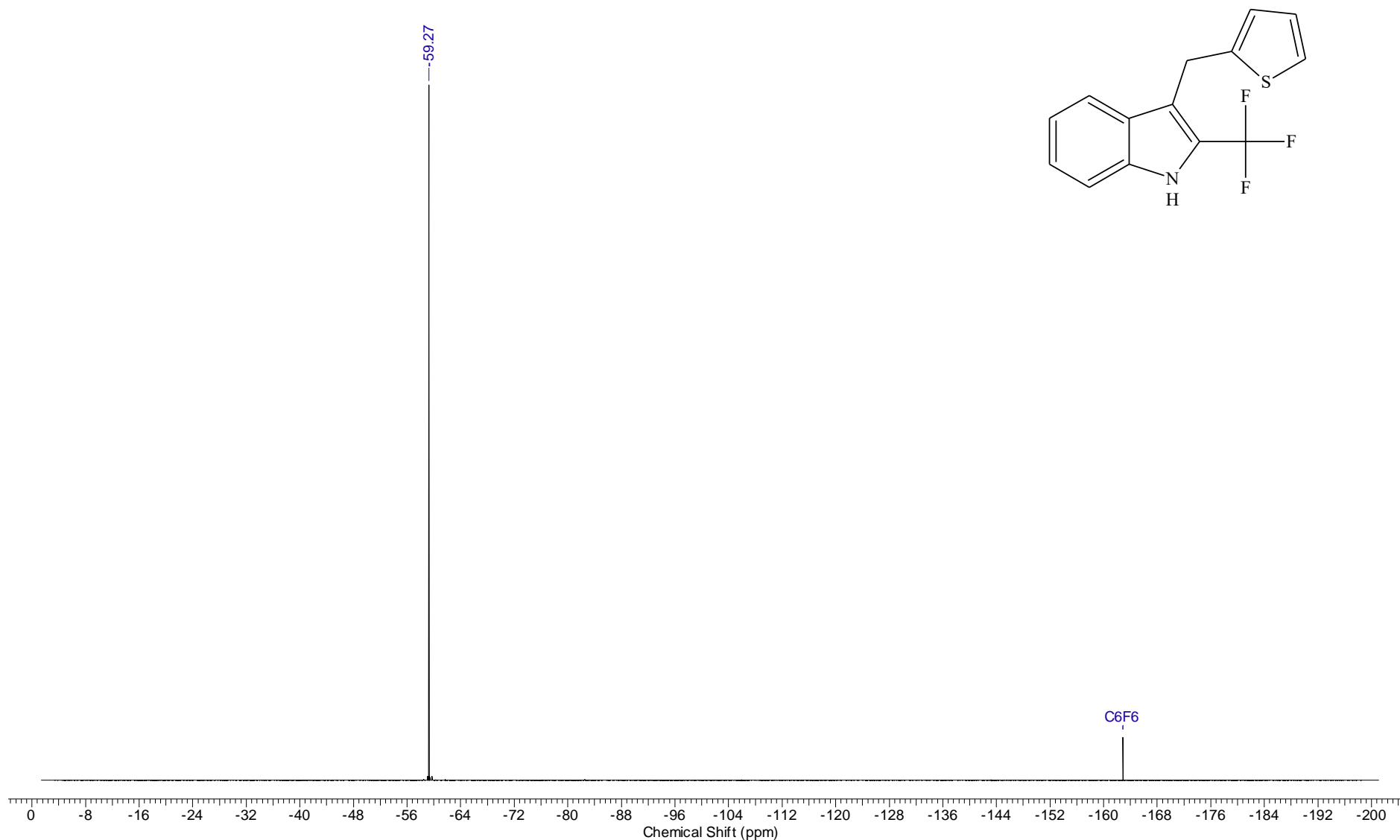


$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4q** (100.6 MHz,  $\text{CDCl}_3$ )

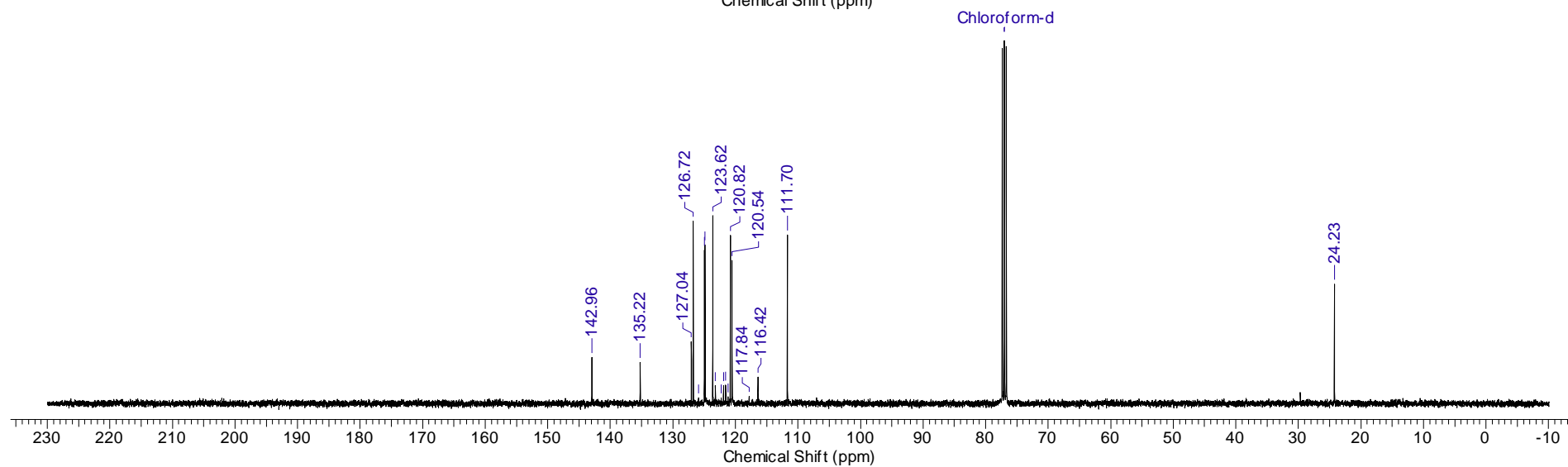
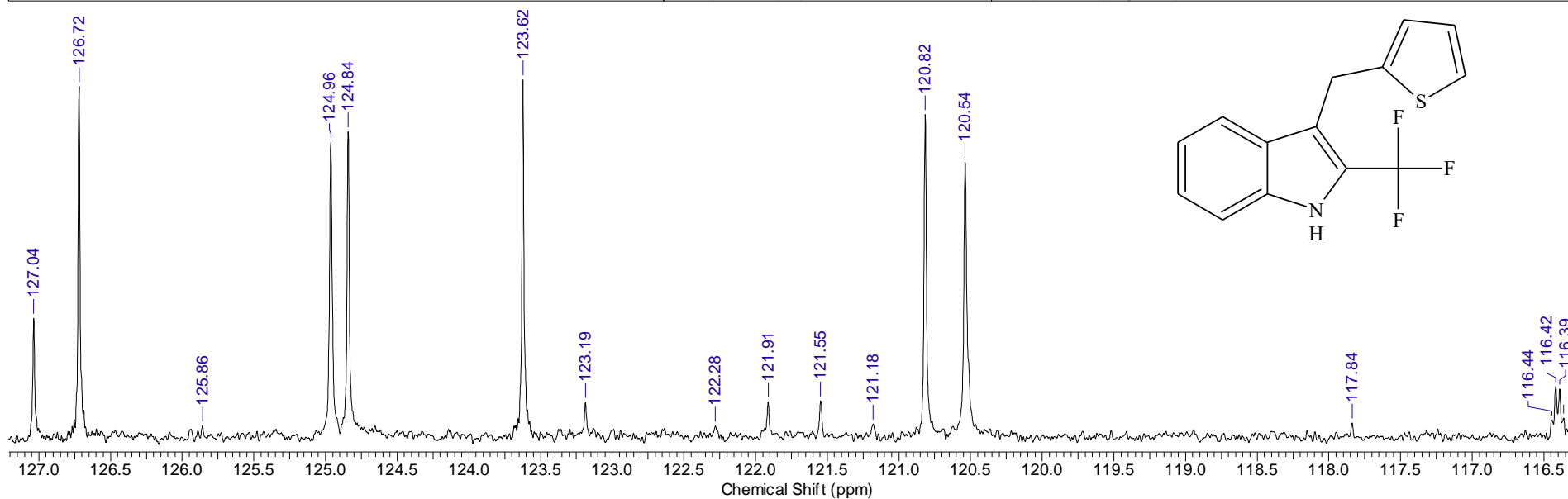
|                        |   |                      |                      |                       |                 |                        |        |
|------------------------|---|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 4.0894  | Comment              | Imported from UXNMR. |                       | Date            | 30 Mar 2021 14:49:28   |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\03.羰菲\BM-2116-1.H_001001r |                      |                      |                       | Frequency (MHz) | 400.13                 |        |
| Nucleus                | 1H  | Number of Transients | 4                    | Original Points Count | 32768           | Points Count           | 131072 |
| Pulse Sequence         | zg30  | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 8012.82         | Temperature (degree C) | 27.000 |

<sup>1</sup>H NMR spectrum of **4r** (400.1 MHz, CDCl<sub>3</sub>)

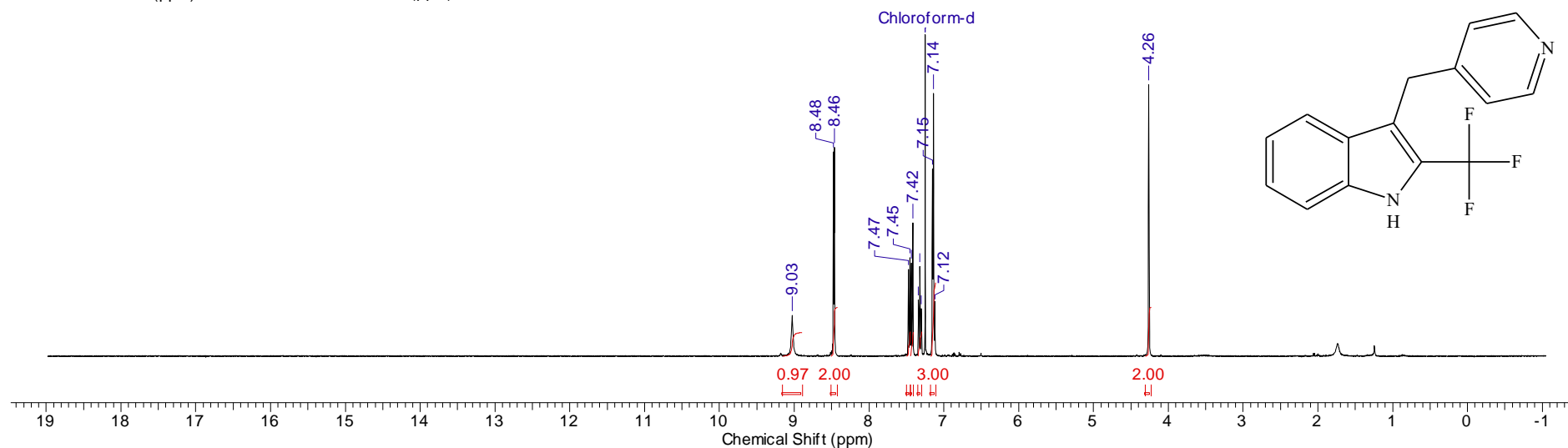
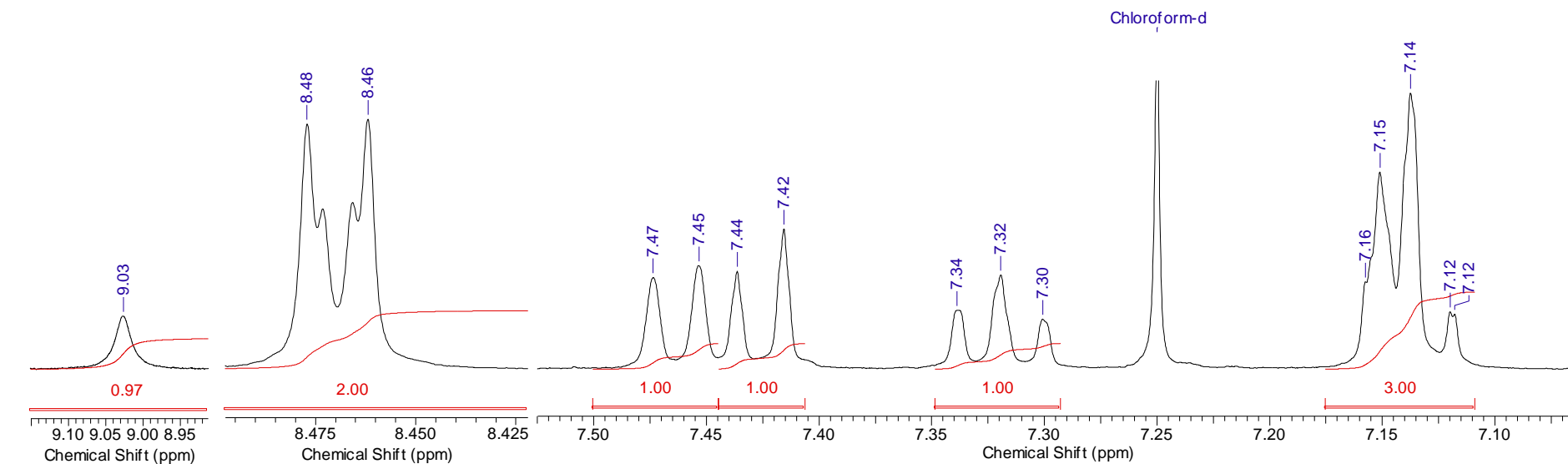
|                        |   |                      |                      |                       |          |                        |                      |
|------------------------|---|----------------------|----------------------|-----------------------|----------|------------------------|----------------------|
| Acquisition Time (sec) | 1.7433  | Comment              | Imported from UXNMR. |                       |          | Date                   | 30 Mar 2021 15:52:02 |
| File Name              | C:\DOCS\OUTPUT_301\2021\03 羰基\BM-2116-1.F_005001r |                      |                      |                       |          | Frequency (MHz)        | 376.50               |
| Nucleus                | 19F   | Number of Transients | 11                   | Original Points Count | 131072   | Points Count           | 262144               |
| Pulse Sequence         | zgfgqn  | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 75187.97 | Temperature (degree C) | 27.000               |



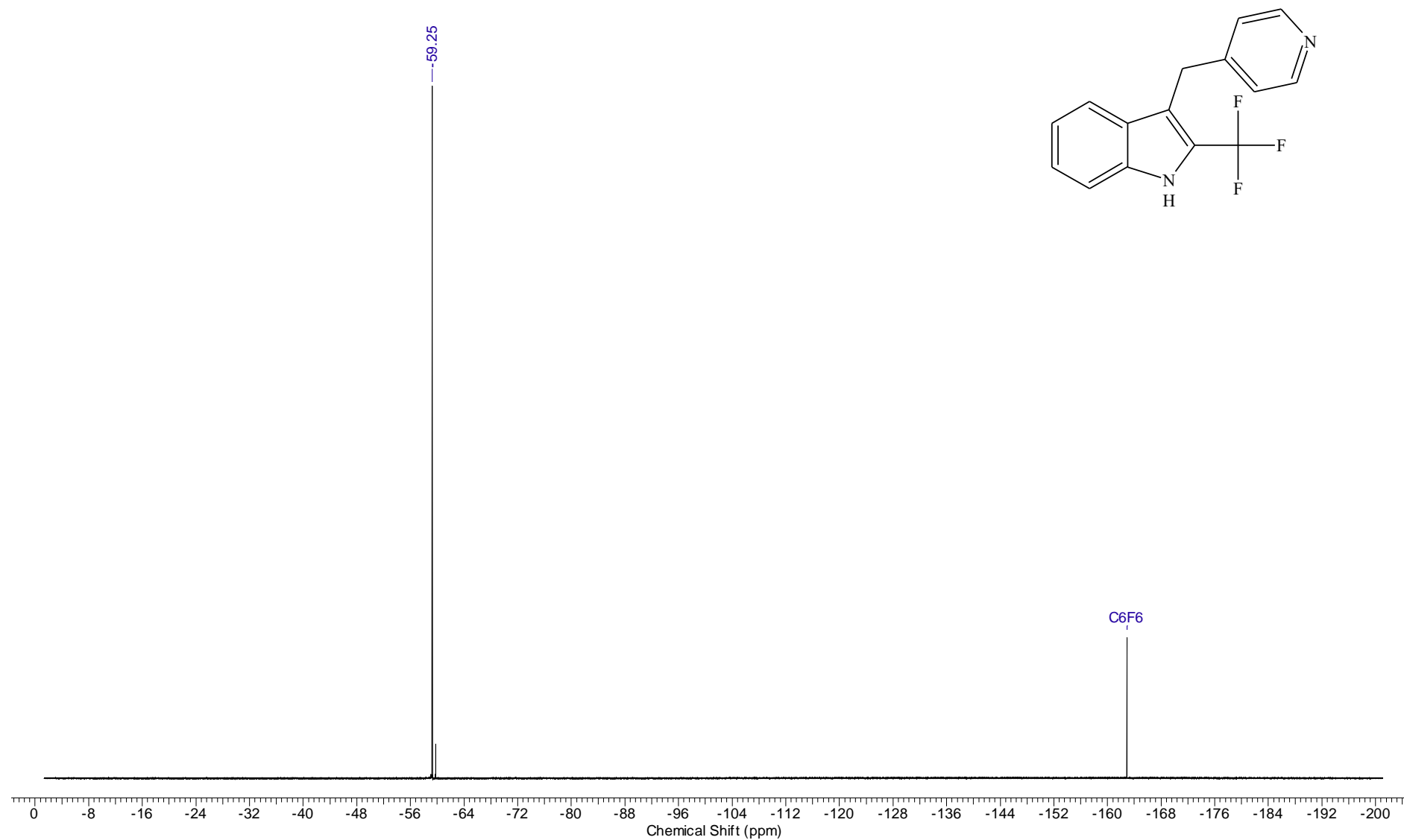
|                        |   |                       |                      |  |                        |                      |  |
|------------------------|---|-----------------------|----------------------|--|------------------------|----------------------|--|
| Acquisition Time (sec) | 0.6783  | Comment               | Imported from Uxnmr. |  | Date                   | 30 Mar 2021 15:06:26 |  |
| File Name              | C:\DOCS\OUTPUT_301\2021\03\羰菲\BM-2116-1.C_002001r | Frequency (MHz)       | 100.61               |  | Nucleus                | 13C                  |  |
| Number of Transients   | 433   | Original Points Count | 16384                |  | Pulse Sequence         | zgpg30               |  |
| Solvent                | CHLOROFORM-D                                      | Sweep Width (Hz)      | 24154.59             |  | Temperature (degree C) | 27.000               |  |

 $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4r** (100.6 MHz,  $\text{CDCl}_3$ )

|                        |  |                      |                      |                       |       |                  |                      |
|------------------------|--|----------------------|----------------------|-----------------------|-------|------------------|----------------------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UXNMR. |                       |       | Date             | 18 Mar 2021 12:10:04 |
| File Name              | C:\DOCS\OUTPUT_301\2021\03 羰基BM-2104-C.H_001001r |                      |                      |                       |       | Frequency (MHz)  | 400.13               |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768 | Points Count     | 131072               |
| Pulse Sequence         | zg30   | Solvent              | CHLOROFORM-D         |                       |       | Sweep Width (Hz) | 8012.82              |
| Temperature (degree C) | 27.000   |                      |                      |                       |       |                  |                      |

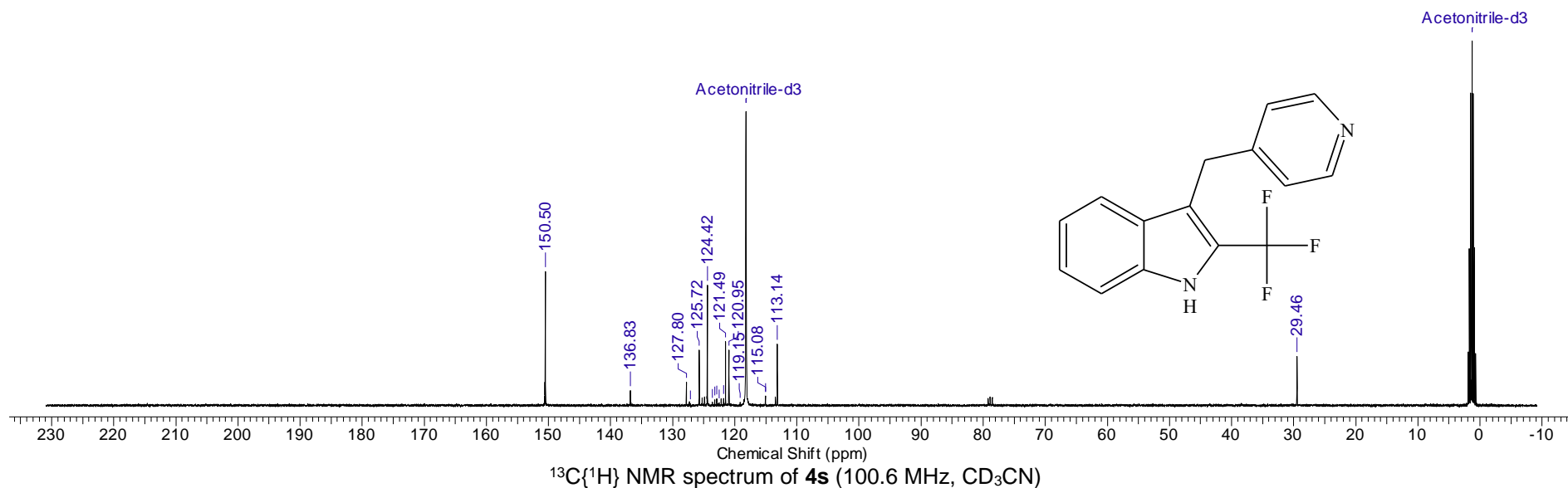
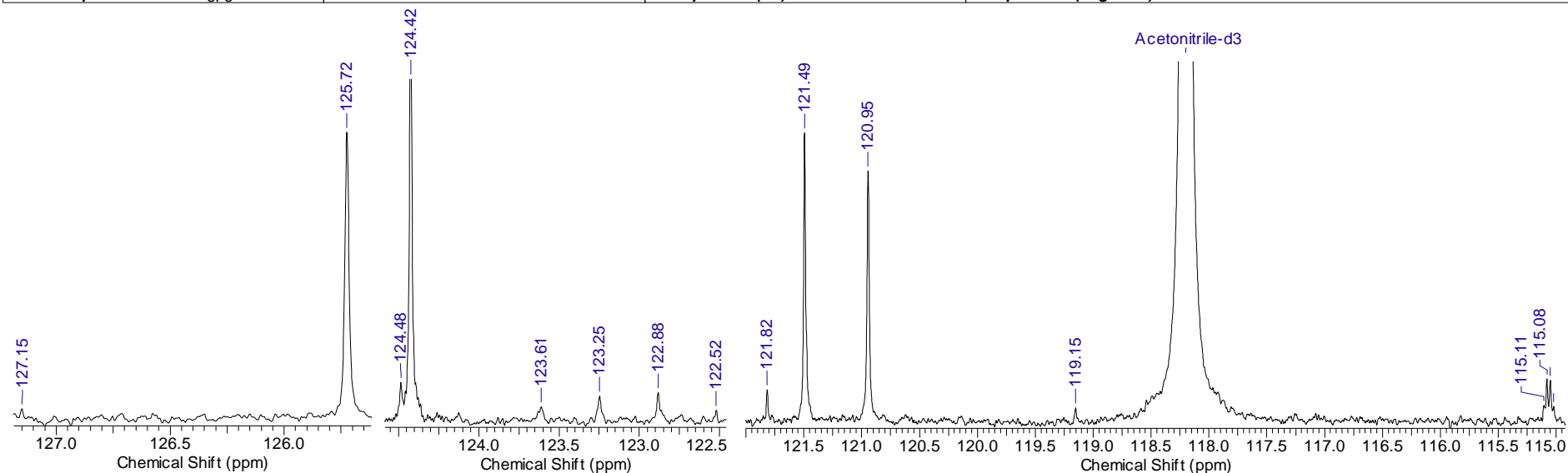
<sup>1</sup>H NMR spectrum of **4s** (400.1 MHz, CD<sub>3</sub>CN)

|                               |  |                              |                      |                               |             |                             |
|-------------------------------|--|------------------------------|----------------------|-------------------------------|-------------|-----------------------------|
| <b>Acquisition Time (sec)</b> | 1.7433   | <b>Comment</b>               | Imported from UXNMR. |                               | <b>Date</b> | 18 Mar 2021 13:06:30        |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2021\03 羰基BM-2104-C.F_005001r | <b>Frequency (MHz)</b>       | 376.50               | <b>Nucleus</b>                | 19F         |                             |
| <b>Number of Transients</b>   | 16   | <b>Original Points Count</b> | 131072               | <b>Points Count</b>           | 262144      | <b>Pulse Sequence</b> zgfgn |
| <b>Solvent</b>                | CHLOROFORM-D                                     | <b>Sweep Width (Hz)</b>      | 75187.97             | <b>Temperature (degree C)</b> | 27.000      |                             |

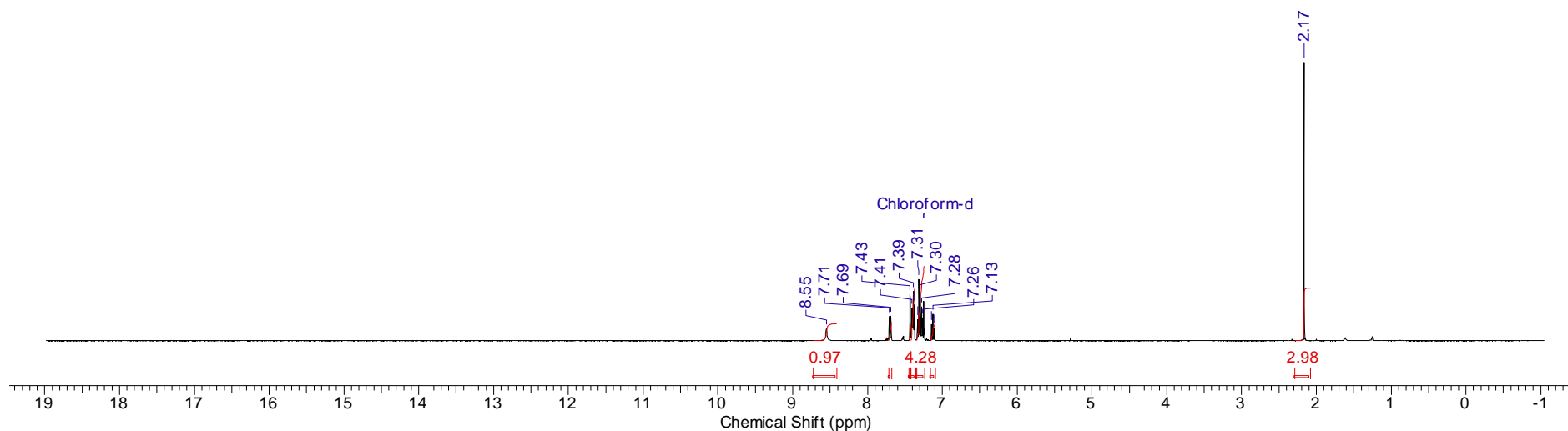
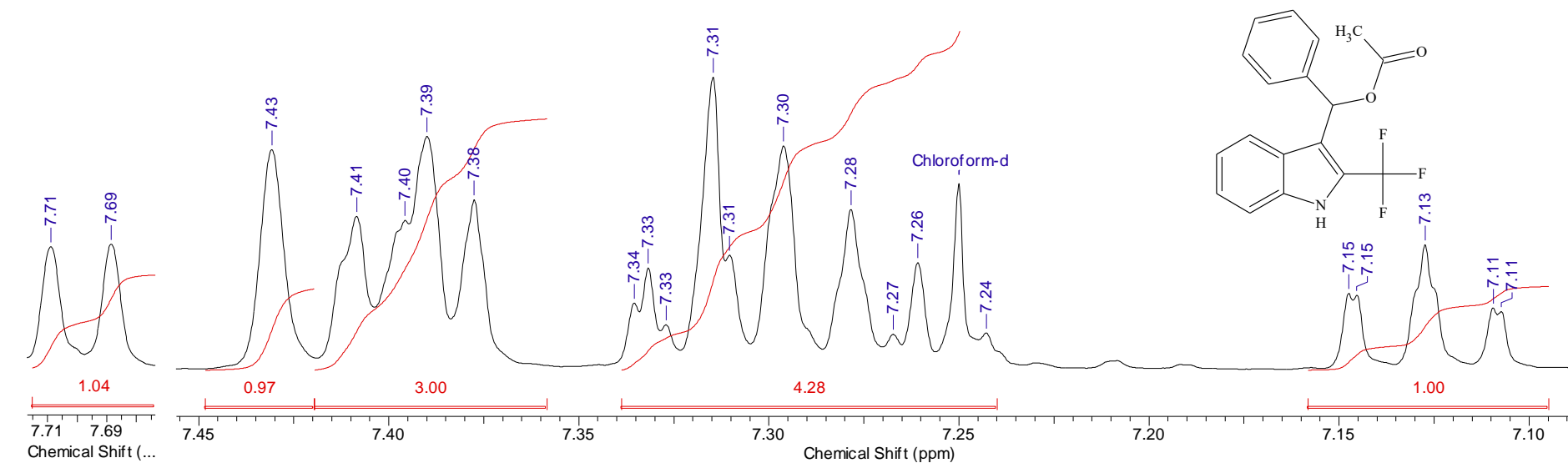




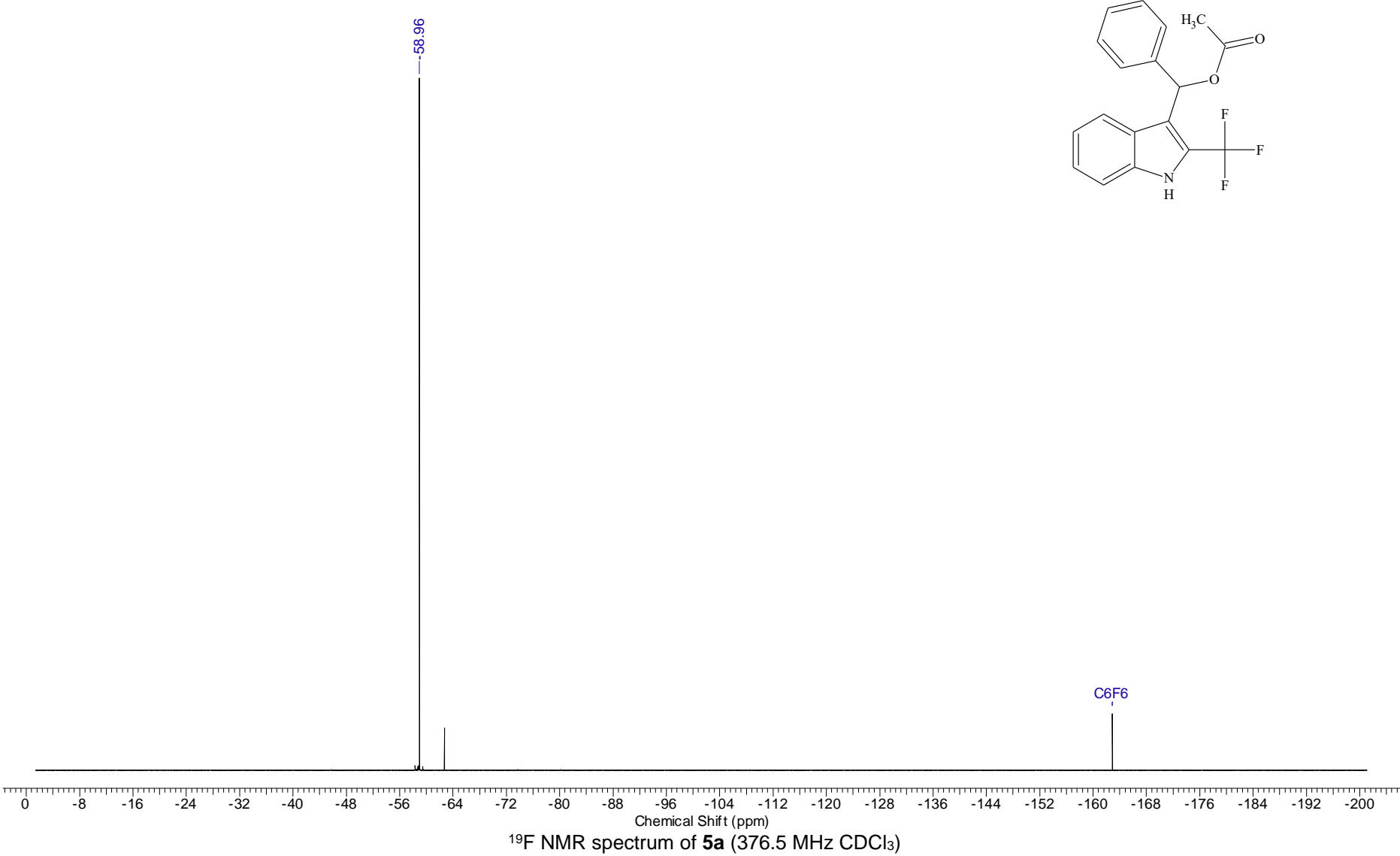
|                        |  |                      |                      |                       |                 |                        |        |
|------------------------|--|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 0.6783   | Comment              | Imported from UXMNR. |                       | Date            | 16 Mar 2021 14:07:26   |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\03 羰基BM-2104-2.C_002001r |                      |                      |                       | Frequency (MHz) | 100.61                 |        |
| Nucleus                | 13C  | Number of Transients | 801                  | Original Points Count | 16384           | Points Count           | 131072 |
| Pulse Sequence         | zgpg30   | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 24154.59        | Temperature (degree C) | 27.000 |



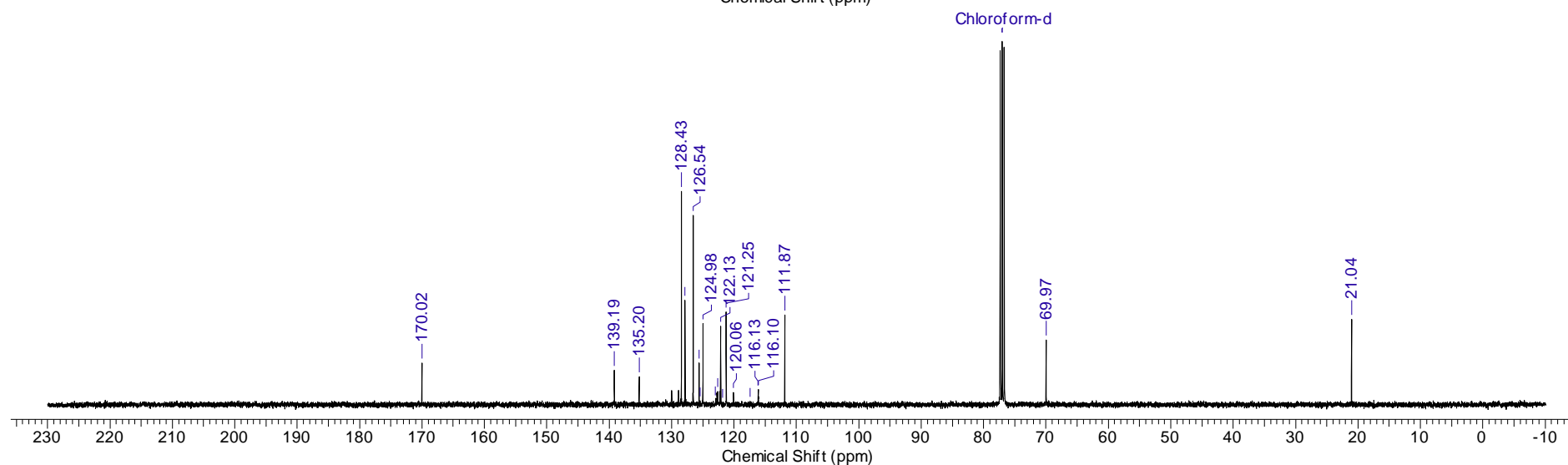
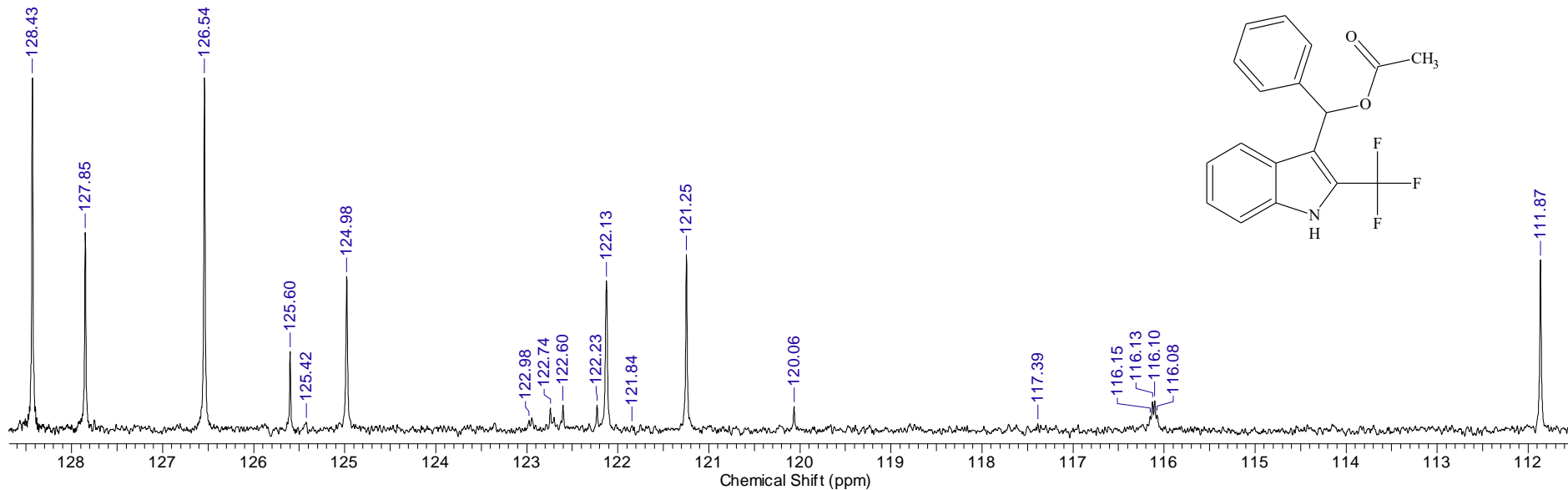
|                        |   |                      |                      |                       |                  |                      |        |
|------------------------|---|----------------------|----------------------|-----------------------|------------------|----------------------|--------|
| Acquisition Time (sec) | 4.0894  | Comment              | Imported from UXNMR. |                       | Date             | 23 Jan 2021 12:24:10 |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\01. 磯田黒BM-2038-3p.H_001001r |                      |                      |                       | Frequency (MHz)  | 400.13               |        |
| Nucleus                | 1H  | Number of Transients | 4                    | Original Points Count | 32768            | Points Count         | 131072 |
| Pulse Sequence         | zg30  | Solvent              | CHLOROFORM-D         |                       | Sweep Width (Hz) | 8012.82              |        |
| Temperature (degree C) | 27.000  |                      |                      |                       |                  |                      |        |

<sup>1</sup>H NMR spectrum of **5a** (400.1 MHz, CDCl<sub>3</sub>)

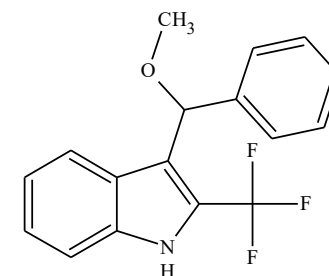
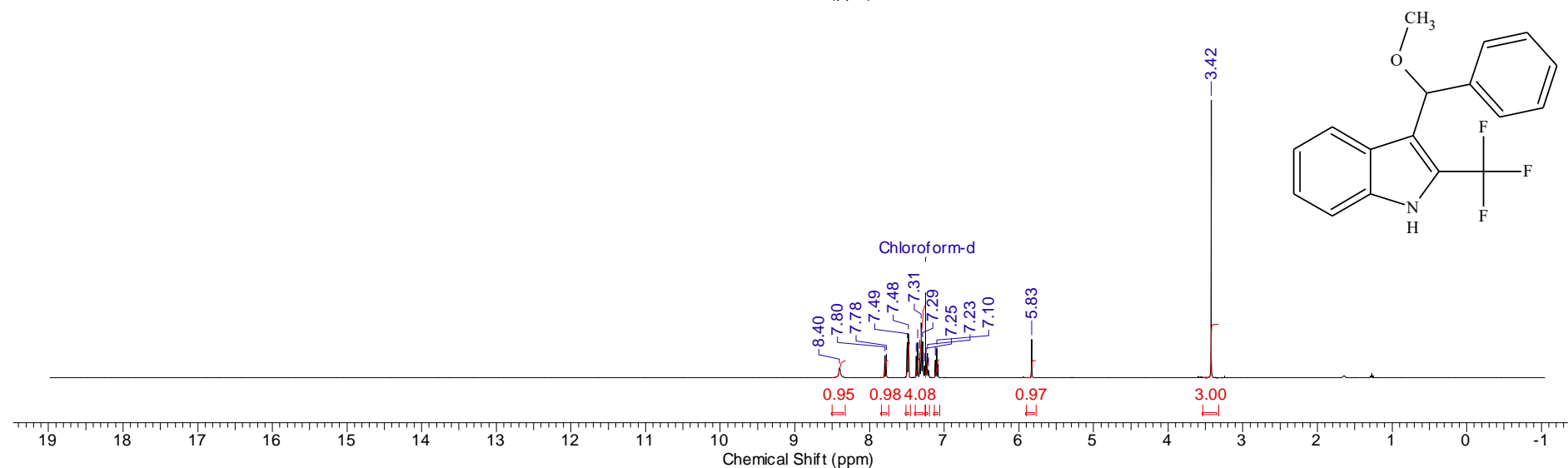
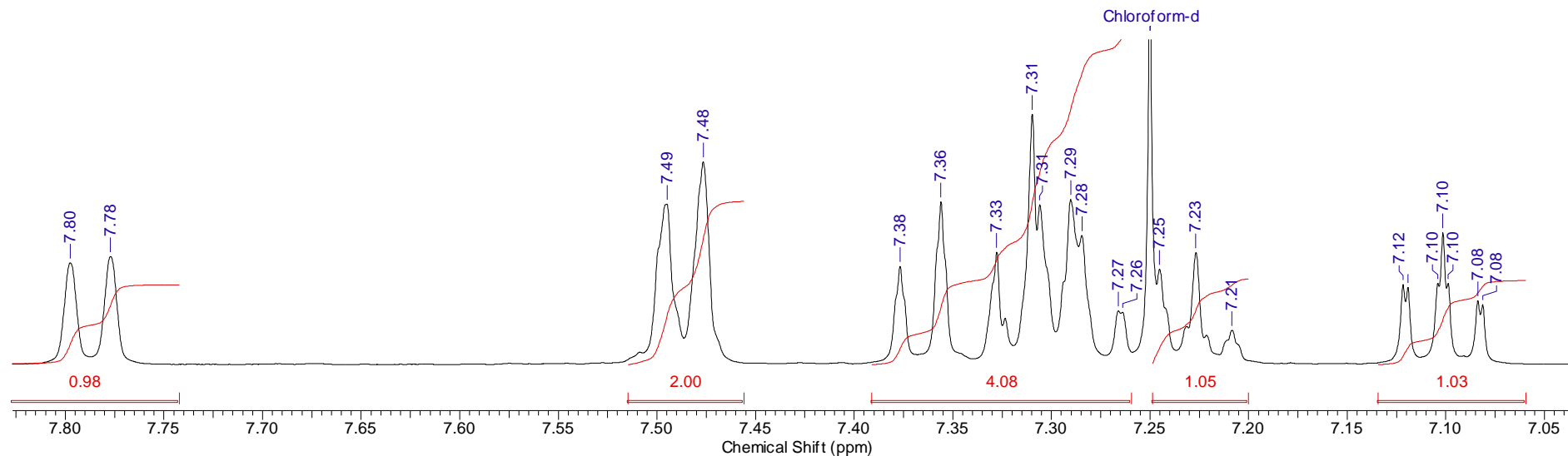
|                               |  |                              |                      |                               |             |                              |
|-------------------------------|--|------------------------------|----------------------|-------------------------------|-------------|------------------------------|
| <b>Acquisition Time (sec)</b> | 1.7433                                 | <b>Comment</b>               | Imported from UXMNR. |                               | <b>Date</b> | 23 Jan 2021 23:10:56         |
| <b>File Name</b>              | C:\DOCS\BM\bm210123\BM-2038-3p_005001r | <b>Frequency (MHz)</b>       | 376.50               | <b>Nucleus</b>                | 19F         |                              |
| <b>Number of Transients</b>   | 16                                     | <b>Original Points Count</b> | 131072               | <b>Points Count</b>           | 262144      | <b>Pulse Sequence</b> zgfgqn |
| <b>Solvent</b>                | CHLOROFORM-D                           | <b>Sweep Width (Hz)</b>      | 75187.97             | <b>Temperature (degree C)</b> | 27.000      |                              |



|                        |   |                      |                      |                       |                 |                        |        |
|------------------------|---|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 0.6783  | Comment              | Imported from UXMNR. |                       | Date            | 26 Jan 2021 16:10:22   |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\01. 磯岡黒BM-2038-3p.C_002001r |                      |                      |                       | Frequency (MHz) | 100.61                 |        |
| Nucleus                | 13C   | Number of Transients | 929                  | Original Points Count | 16384           | Points Count           | 131072 |
| Pulse Sequence         | zgpg30  | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 24154.59        | Temperature (degree C) | 27.000 |

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **5a** (100.6 MHz, CDCl<sub>3</sub>)

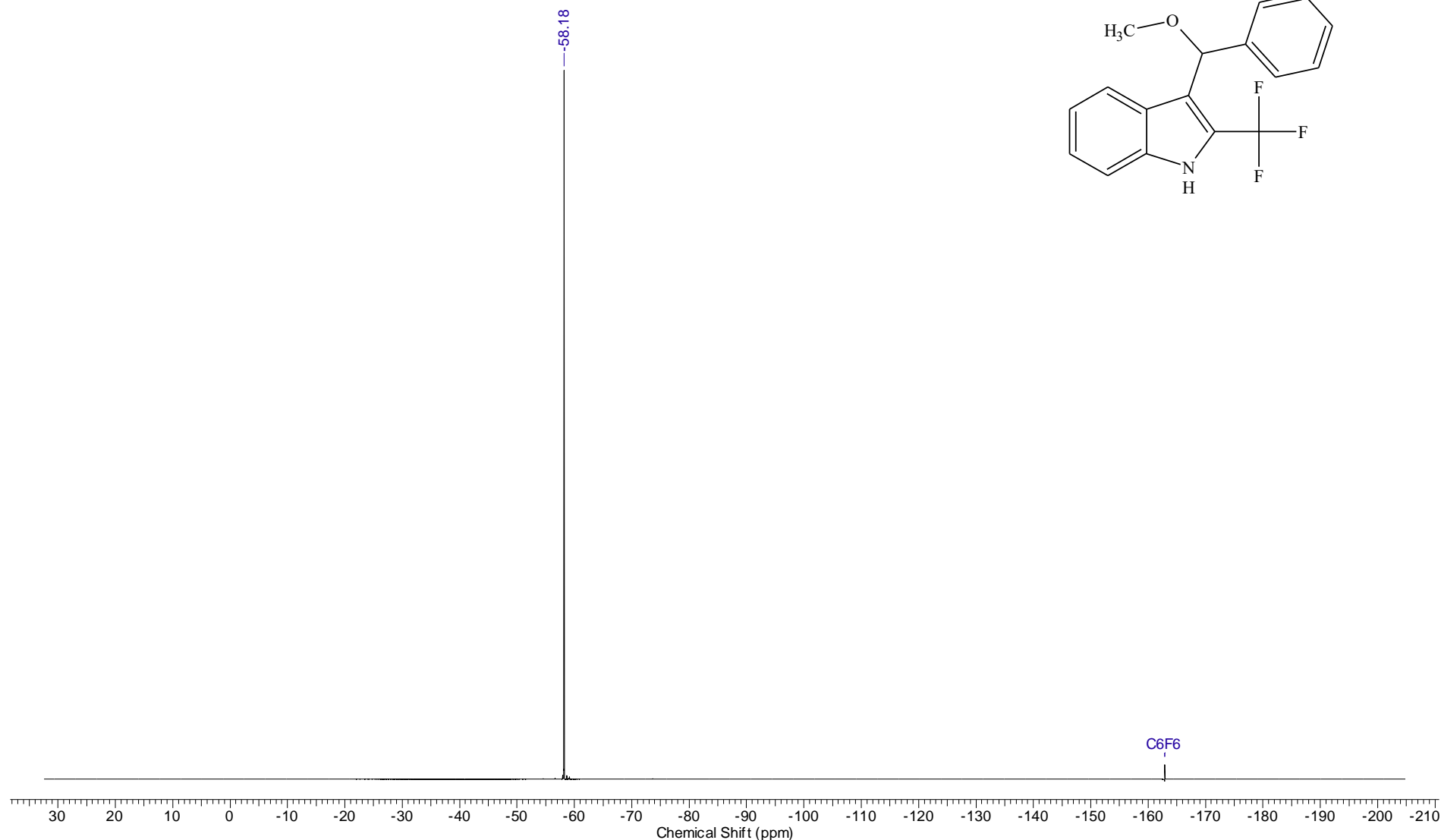
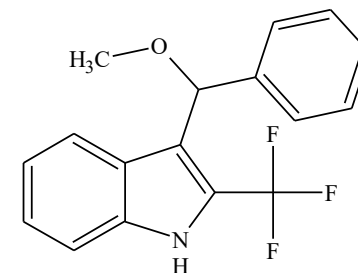
|                        |  |                      |                      |                       |       |                  |                      |
|------------------------|--|----------------------|----------------------|-----------------------|-------|------------------|----------------------|
| Acquisition Time (sec) | 4.0894   | Comment              | Imported from UXNMR. |                       |       | Date             | 06 Nov 2020 15:46:12 |
| File Name              | C:\DOCS\OUTPUT_301\2020\11.脛 狙黒BM-1950.H_001001r |                      |                      |                       |       | Frequency (MHz)  | 400.13               |
| Nucleus                | 1H   | Number of Transients | 4                    | Original Points Count | 32768 | Points Count     | 131072               |
| Pulse Sequence         | zg30   | Solvent              | CHLOROFORM-D         |                       |       | Sweep Width (Hz) | 8012.82              |
| Temperature (degree C) | 27.000   |                      |                      |                       |       |                  |                      |



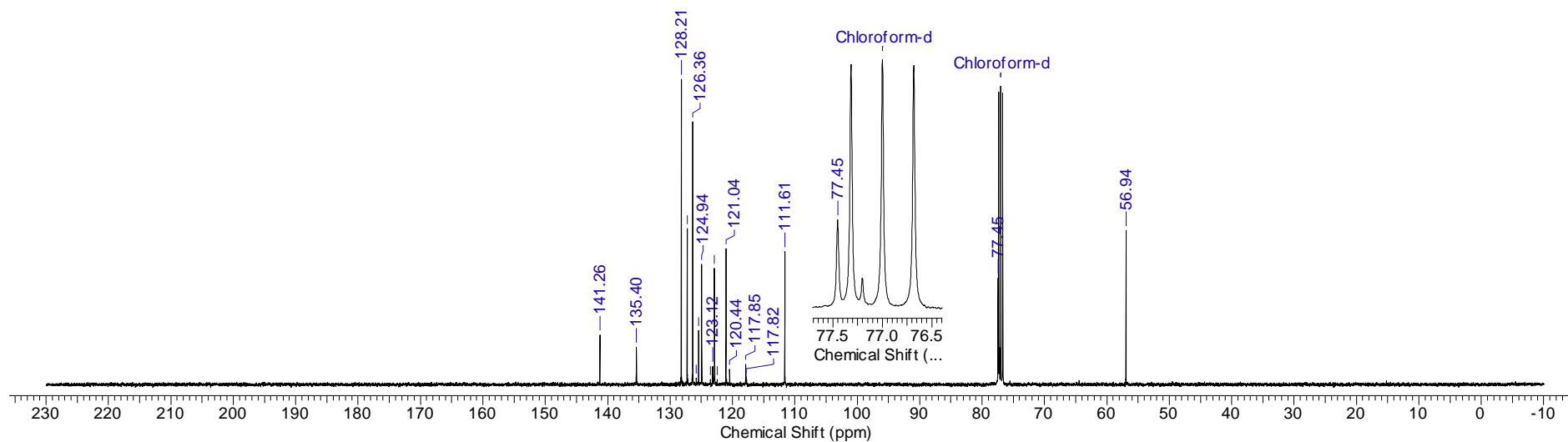
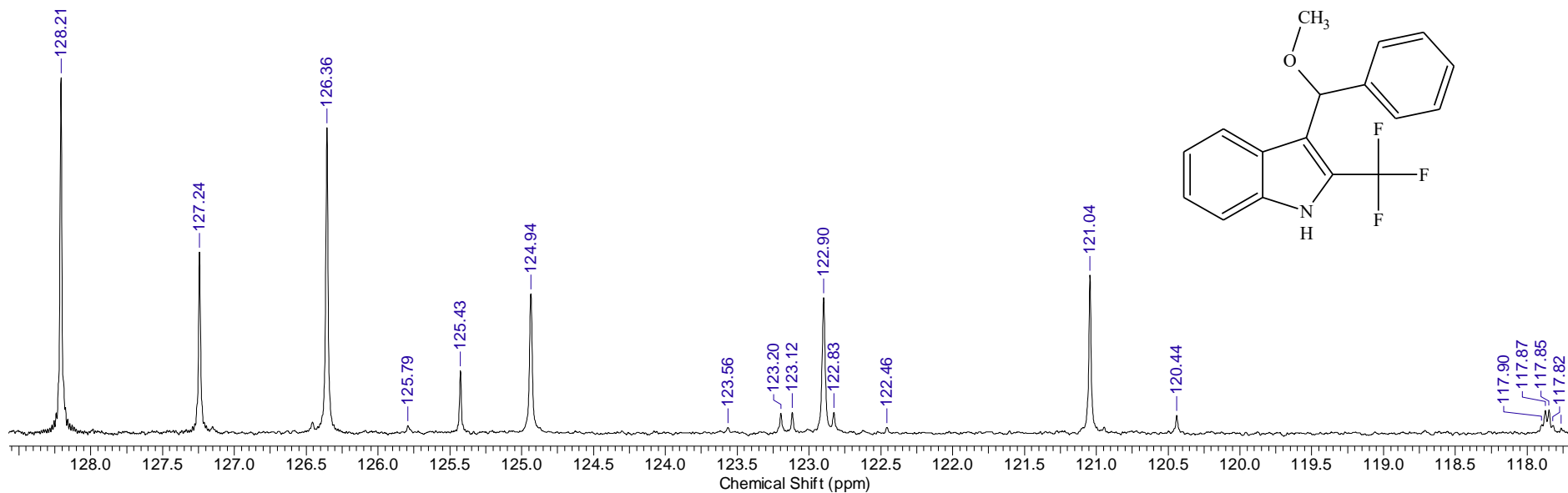
<sup>1</sup>H NMR spectrum of **6a** (400.1 MHz, CDCl<sub>3</sub>)

9 Jun 2021

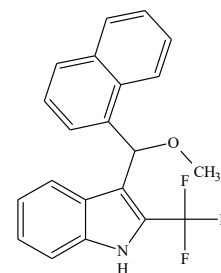
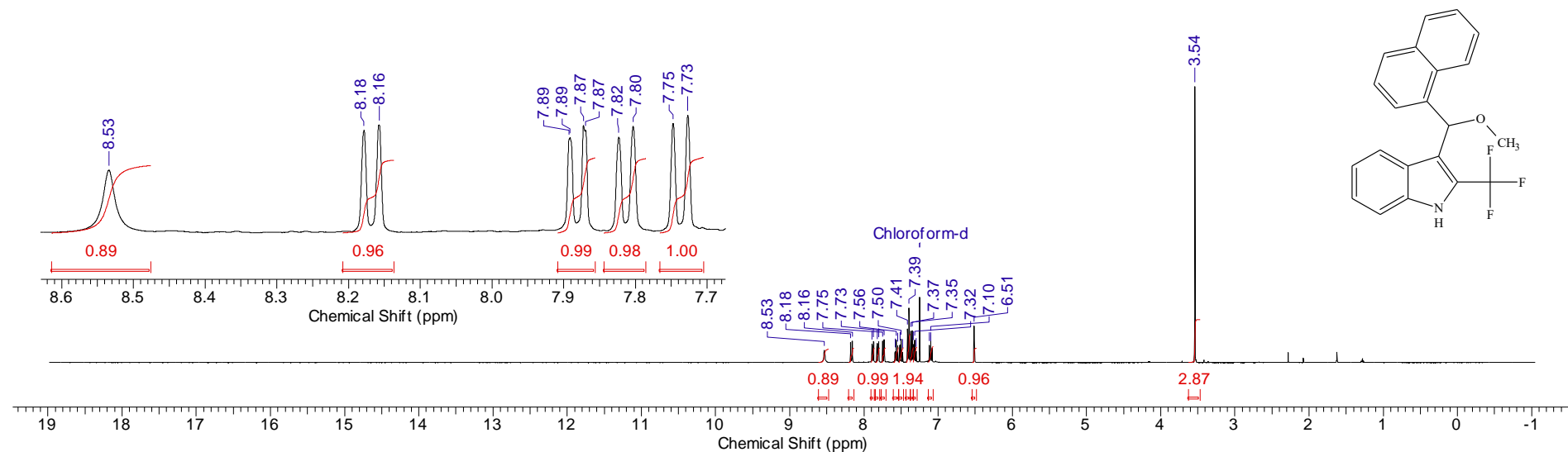
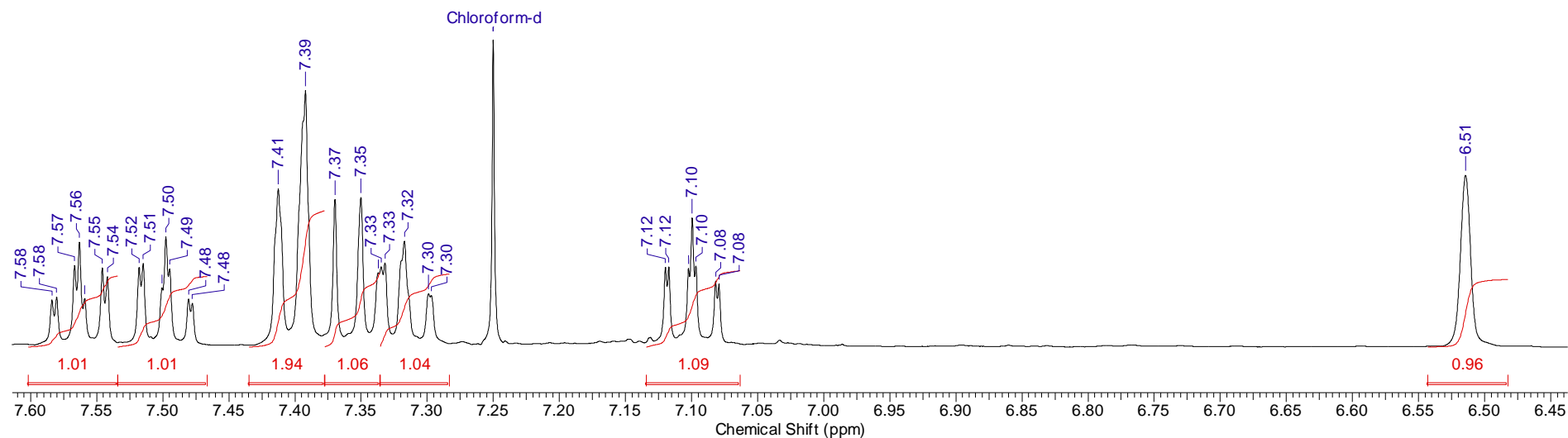
|                        |          |                        |            |                      |   |                             |
|------------------------|----------|------------------------|------------|----------------------|---|-----------------------------|
| Acquisition Time (sec) | 1.0000   | Date                   | Nov 9 2020 | File Name            | C:\DOCS\OUTPUT_301\F19\2020.11.09\BM-1950_20201109_01\FLUORINE_01 |                             |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F        | Number of Transients | 16  | Original Points Count 89286 |
| Points Count           | 131072   | Pulse Sequence         | s2pul      | Solvent              | CHLOROFORM-D  |                             |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 24.000     |                      |   |                             |



|                        |                                      |                       |                      |              |                        |                      |        |
|------------------------|--------------------------------------|-----------------------|----------------------|--------------|------------------------|----------------------|--------|
| Acquisition Time (sec) | 0.6783                               | Comment               | Imported from UXMNR. |              | Date                   | 07 Nov 2020 13:25:40 |        |
| File Name              | C:\DOCS\BMBM_spectra\BM-1950_002001r |                       | Frequency (MHz)      | 100.61       | Nucleus                | 13C                  |        |
| Number of Transients   | 1272                                 | Original Points Count | 16384                | Points Count | 131072                 | Pulse Sequence       | zgpg30 |
| Solvent                | CHLOROFORM-D                         |                       | Sweep Width (Hz)     | 24154.59     | Temperature (degree C) | 27.000               |        |

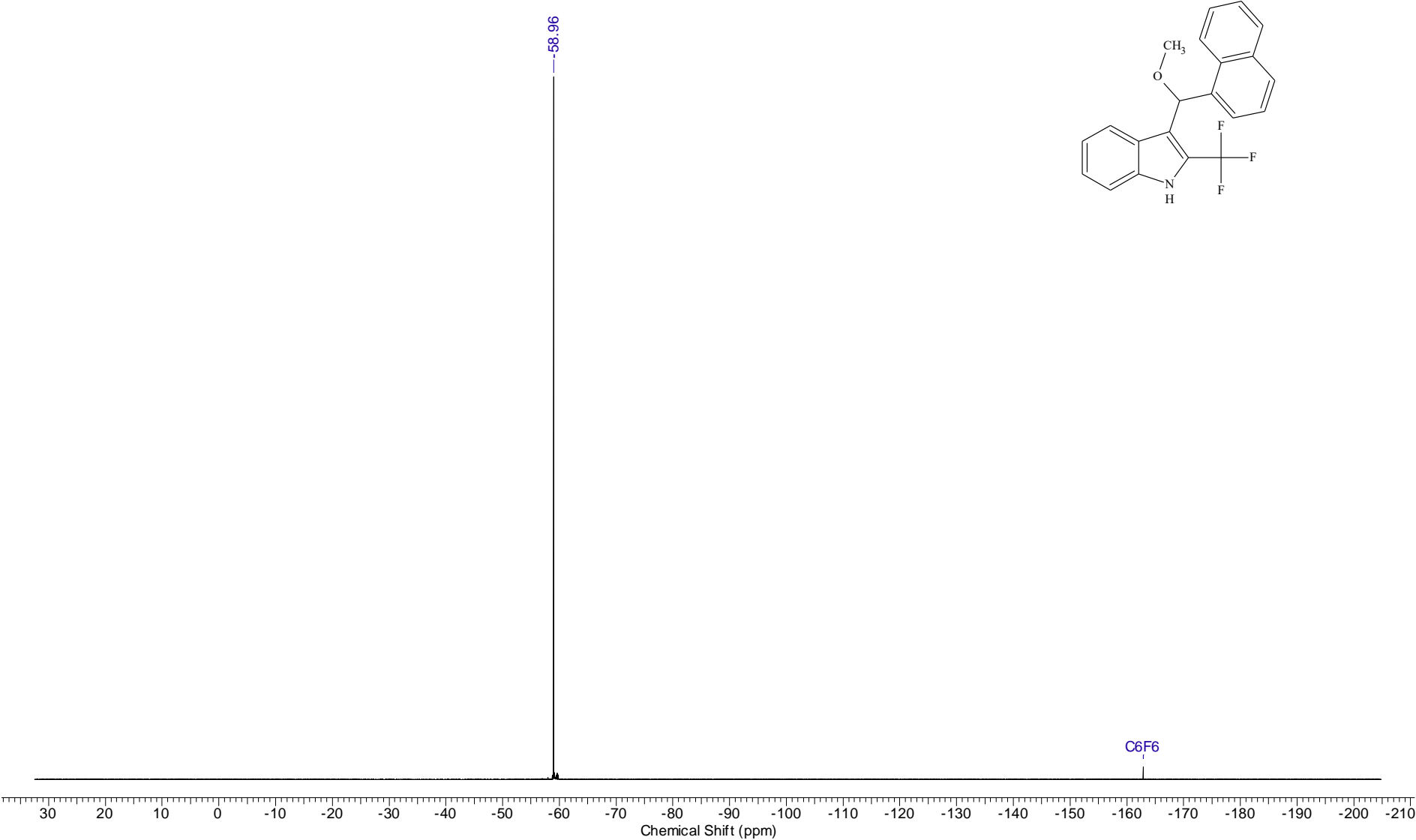
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **6a** (100.6 MHz, CDCl<sub>3</sub>)

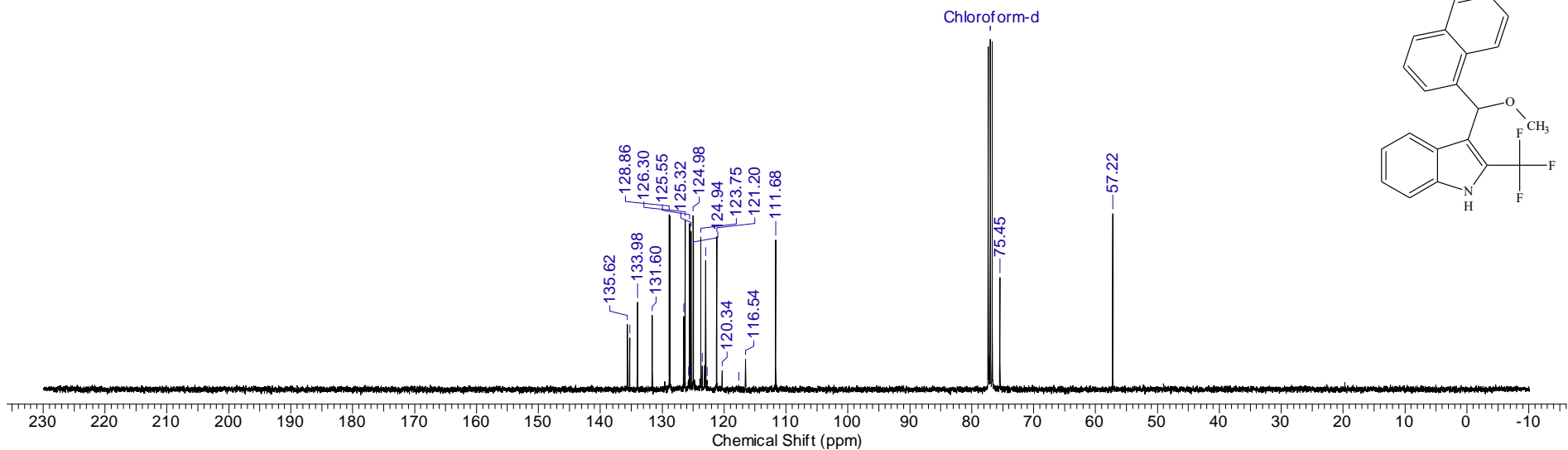
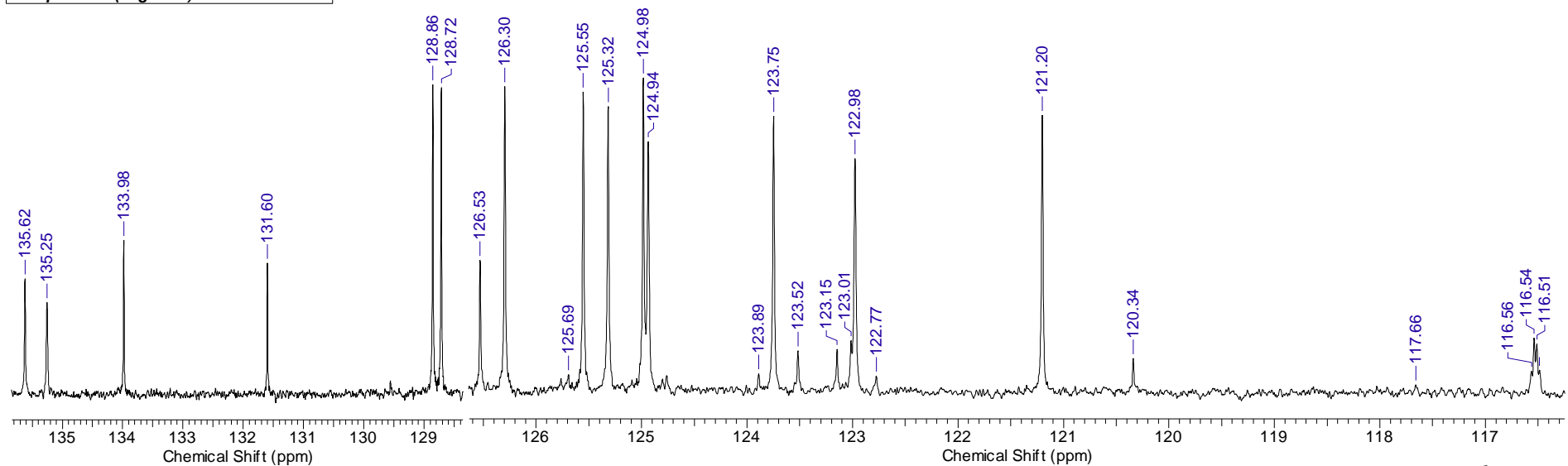
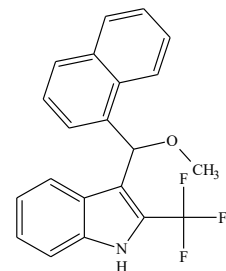
|                               |  |                             |                      |                              |                      |
|-------------------------------|--|-----------------------------|----------------------|------------------------------|----------------------|
| <b>Acquisition Time (sec)</b> | 4.0894   | <b>Comment</b>              | Imported from UXNMR. | <b>Date</b>                  | 03 Dec 2019 14:09:50 |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2019\12\溴赧衍生物\BM-1802-2.H_001001r | <b>Frequency (MHz)</b>      | 400.13               | <b>Points Count</b>          | 131072               |
| <b>Nucleus</b>                | <sup>1</sup> H                                       | <b>Number of Transients</b> | 4                    | <b>Original Points Count</b> | 32768                |
| <b>Pulse Sequence</b>         | zg30   | <b>Solvent</b>              | CHLOROFORM-D         | <b>Sweep Width (Hz)</b>      | 8012.82              |
| <b>Temperature (degree C)</b> | 27.000   |                             |                      |                              |                      |

<sup>1</sup>H NMR spectrum of **6b** (400.1 MHz, CDCl<sub>3</sub>)

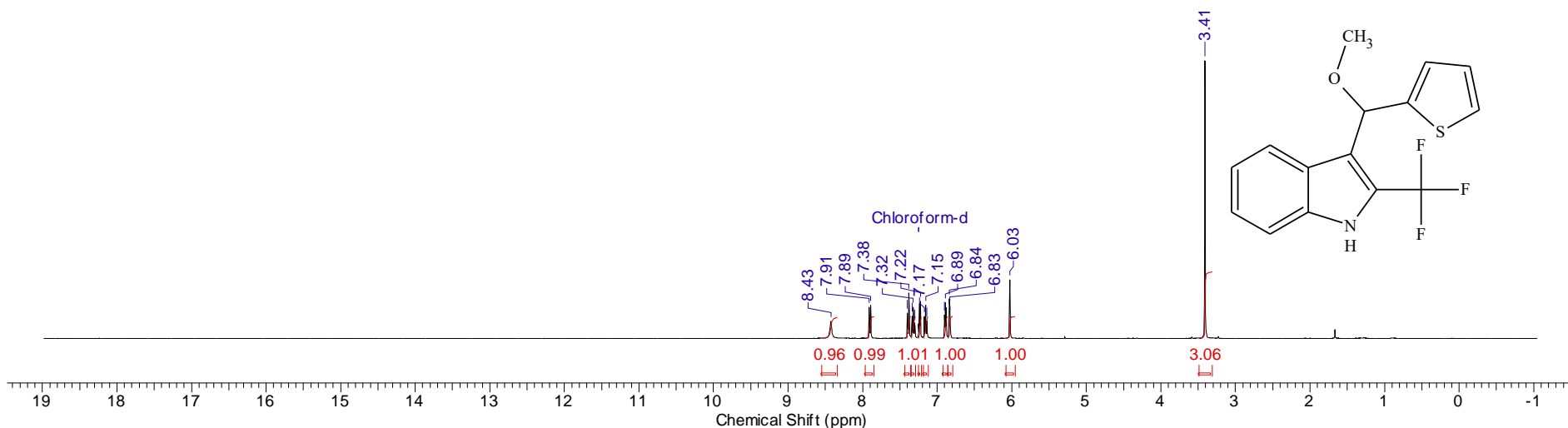
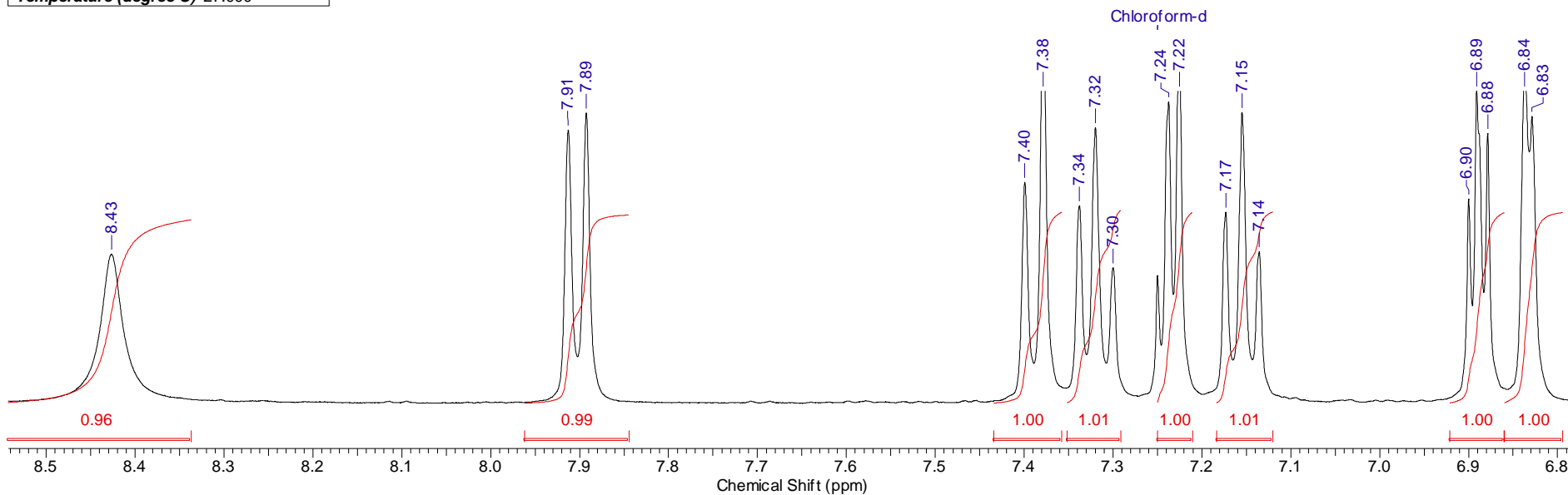


|                        |          |                        |            |                      |   |                              |
|------------------------|----------|------------------------|------------|----------------------|---|------------------------------|
| Acquisition Time (sec) | 2.0000   | Date                   | Dec 2 2019 | File Name            | C:\DOCS\OUTPUT_301\F19\2019.12.02\BM-1802-2_20191202_01\FLUORINE_01 |                              |
| Frequency (MHz)        | 376.31   | Nucleus                | 19F        | Number of Transients | 16  | Original Points Count 178571 |
| Points Count           | 262144   | Pulse Sequence         | s2pul      | Solvent              | CHLOROFORM-D  |                              |
| Sweep Width (Hz)       | 89285.71 | Temperature (degree C) | 22.000     |                      |   |                              |



 $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **6b** (100.6 MHz,  $\text{CDCl}_3$ )

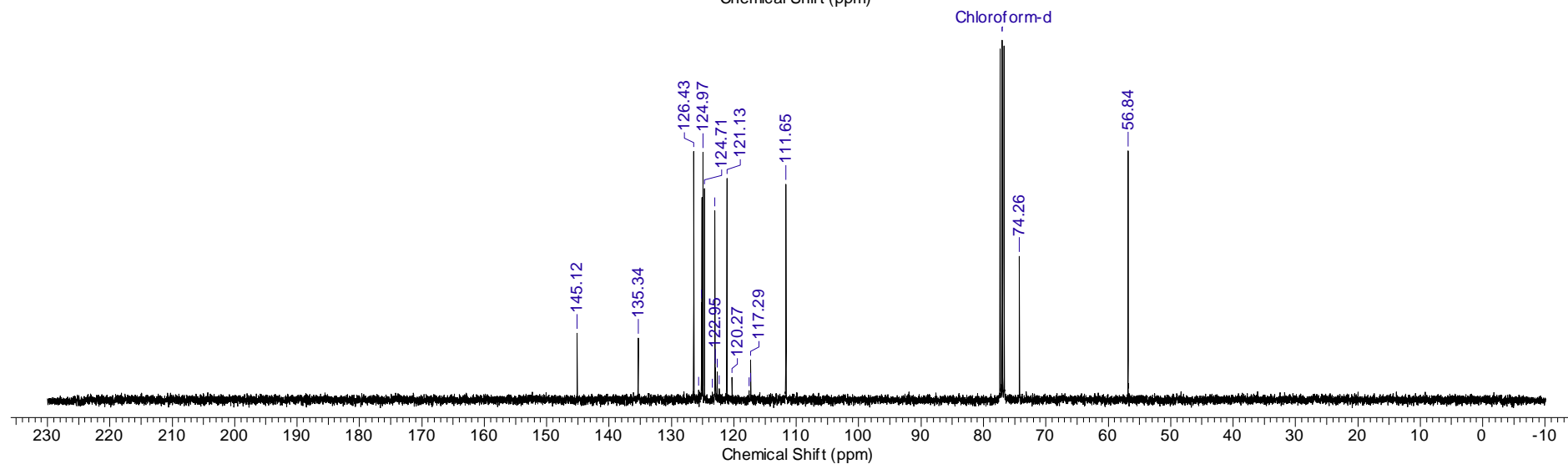
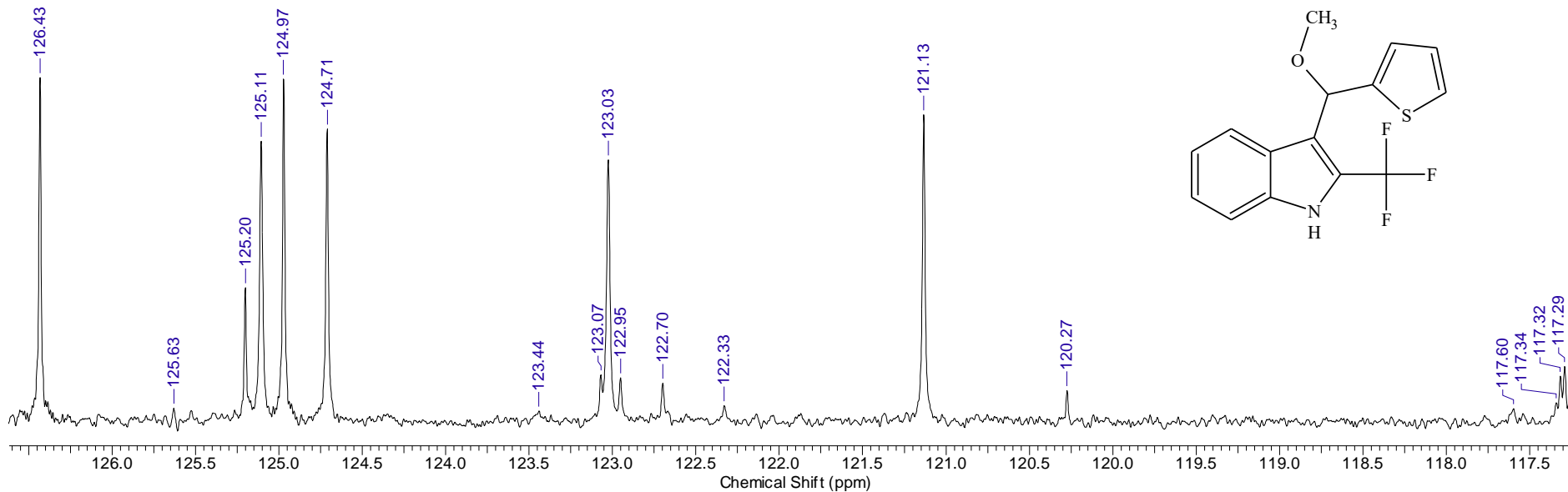
|                        |   |                      |                      |                       |                  |                      |        |
|------------------------|---|----------------------|----------------------|-----------------------|------------------|----------------------|--------|
| Acquisition Time (sec) | 4.0894  | Comment              | Imported from UXMNR. |                       | Date             | 17 Mar 2021 17:45:46 |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\03\墨菲\BM-2108-2.H_001001r |                      |                      |                       | Frequency (MHz)  | 400.13               |        |
| Nucleus                | 1H  | Number of Transients | 4                    | Original Points Count | 32768            | Points Count         | 131072 |
| Pulse Sequence         | zg30  | Solvent              | CHLOROFORM-D         |                       | Sweep Width (Hz) | 8012.82              |        |
| Temperature (degree C) | 27.000  |                      |                      |                       |                  |                      |        |

<sup>1</sup>H NMR spectrum of **6c** (400.1 MHz, CDCl<sub>3</sub>)

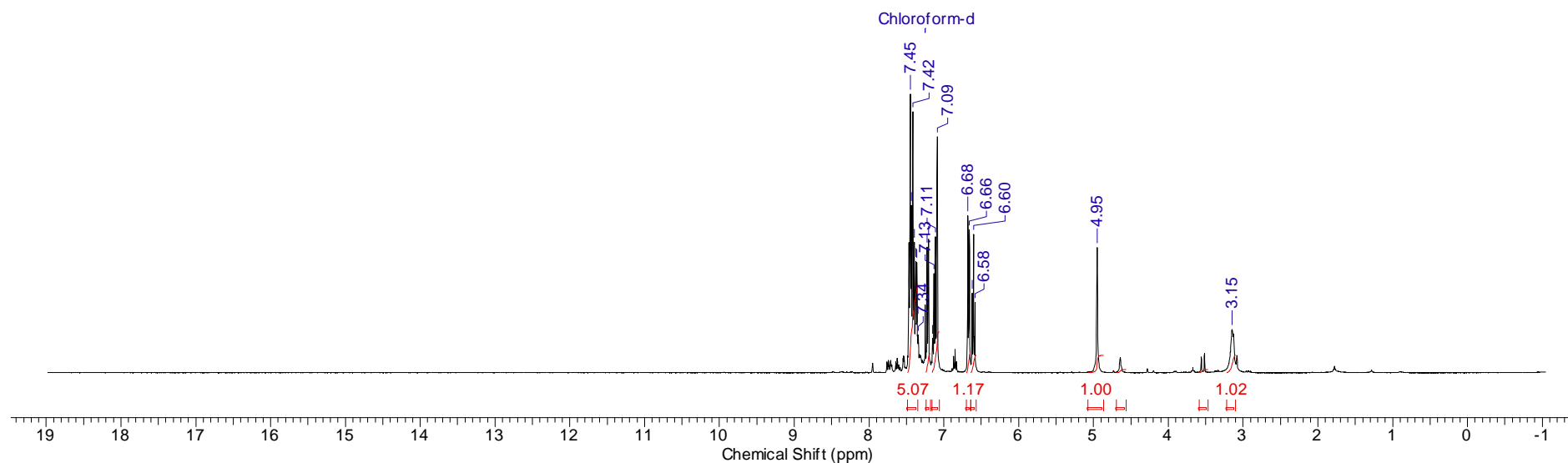
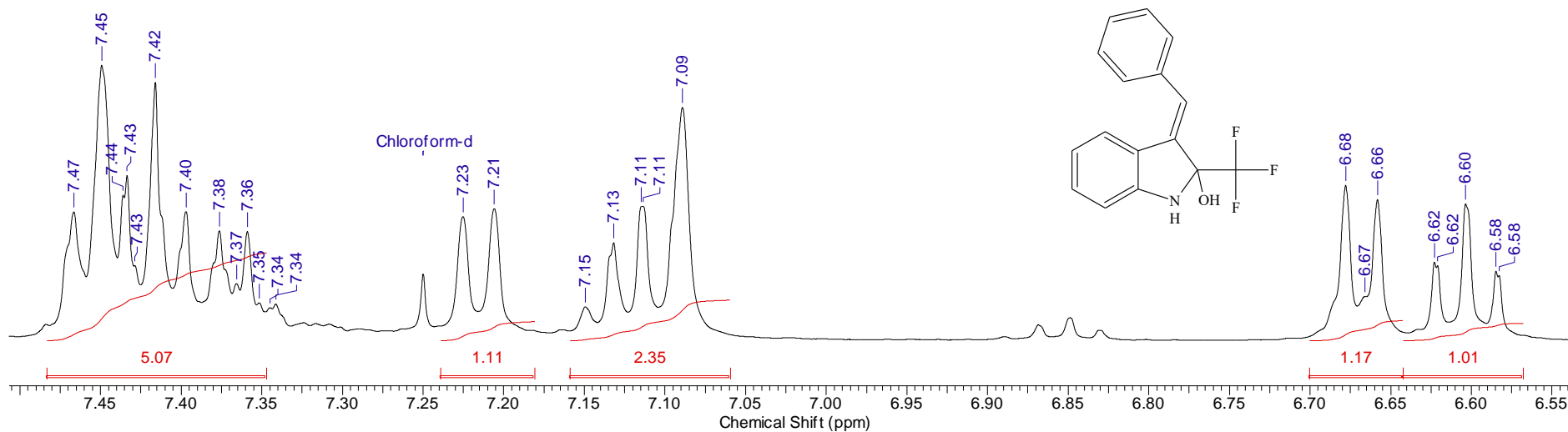
|                               |   |                              |                      |                               |             |                              |
|-------------------------------|---|------------------------------|----------------------|-------------------------------|-------------|------------------------------|
| <b>Acquisition Time (sec)</b> | 1.7433  | <b>Comment</b>               | Imported from UXNMR. |                               | <b>Date</b> | 18 Mar 2021 12:59:50         |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2021\03\羰肼\BM-2108-2.F_005001r | <b>Frequency (MHz)</b>       | 376.50               | <b>Nucleus</b>                | 19F         |                              |
| <b>Number of Transients</b>   | 11  | <b>Original Points Count</b> | 131072               | <b>Points Count</b>           | 262144      | <b>Pulse Sequence</b> zgfgqn |
| <b>Solvent</b>                | CHLOROFORM-D                                      | <b>Sweep Width (Hz)</b>      | 75187.97             | <b>Temperature (degree C)</b> | 27.000      |                              |



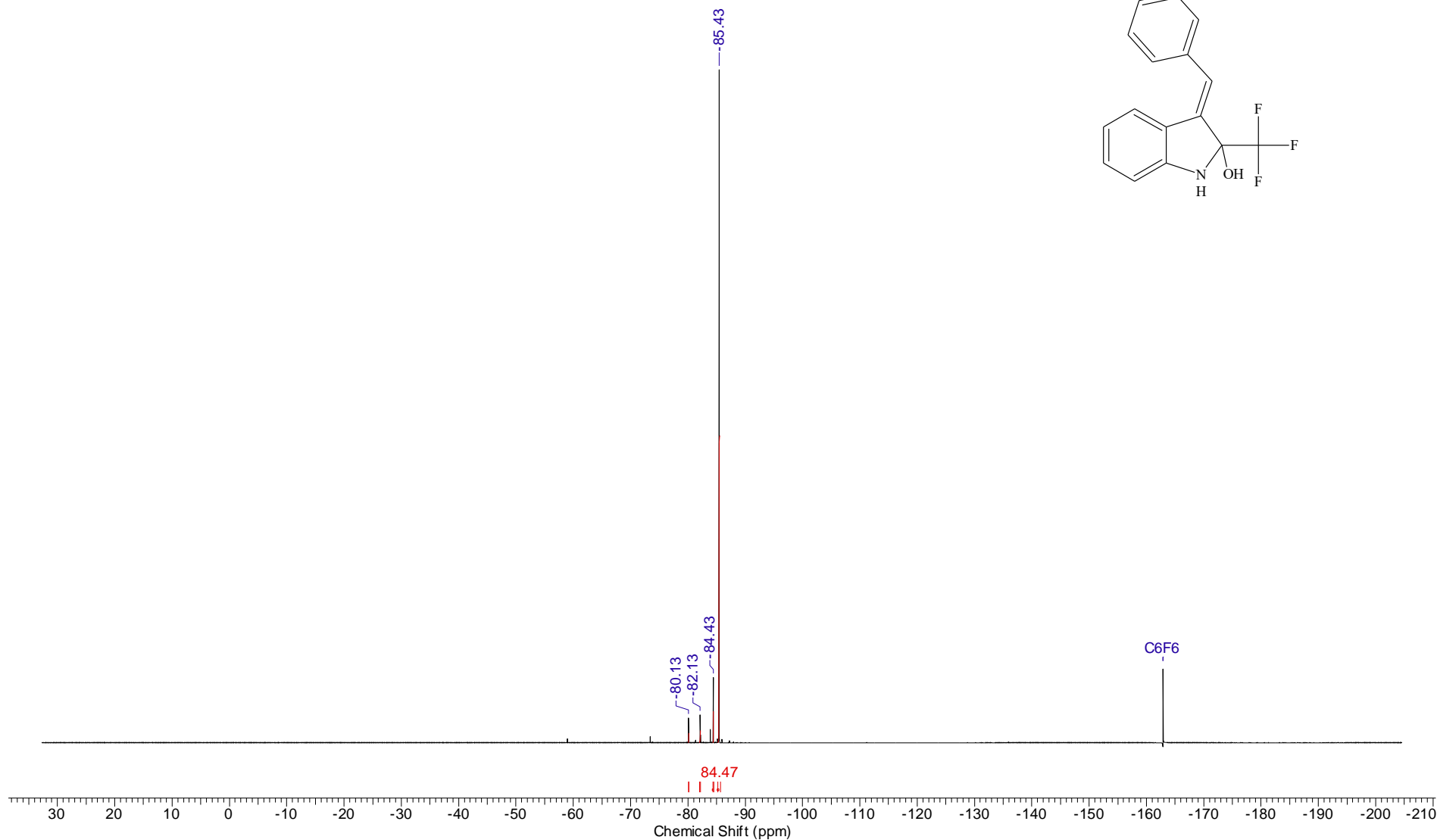
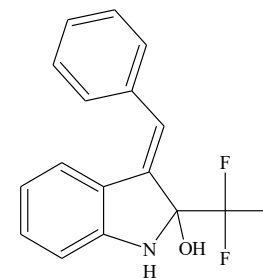
|                        |   |                      |                      |                       |                 |                        |        |
|------------------------|---|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 0.6783  | Comment              | Imported from UXNMR. |                       | Date            | 18 Mar 2021 12:43:52   |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\03 羰基\BM-2108-2.C_002001r |                      |                      |                       | Frequency (MHz) | 100.61                 |        |
| Nucleus                | 13C   | Number of Transients | 265                  | Original Points Count | 16384           | Points Count           | 131072 |
| Pulse Sequence         | zgpg30  | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 24154.59        | Temperature (degree C) | 27.000 |

<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **6c** (100.6 MHz, CDCl<sub>3</sub>)

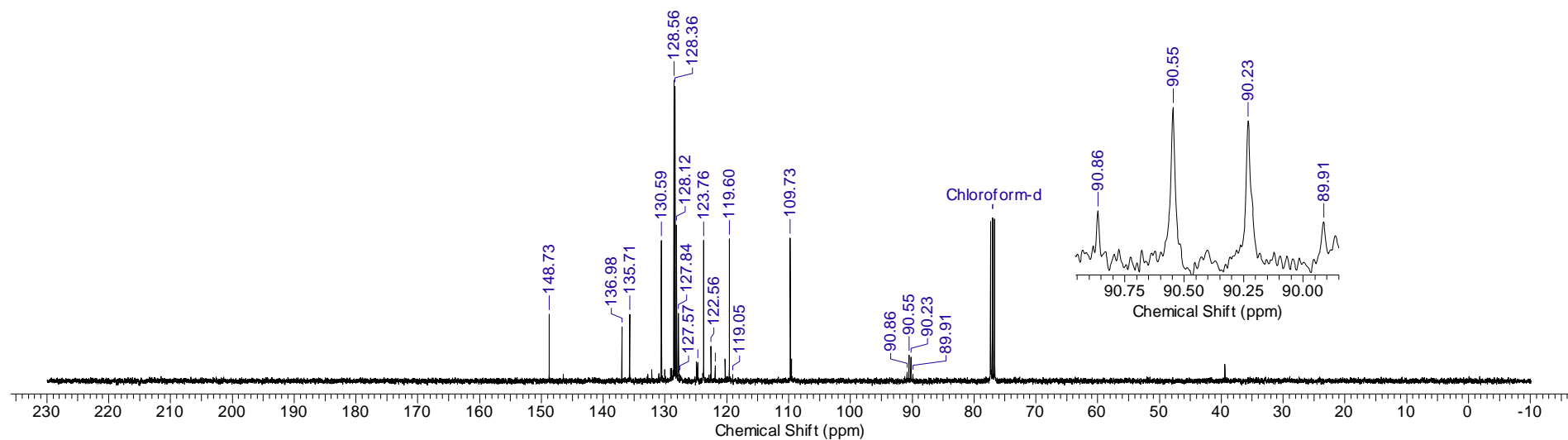
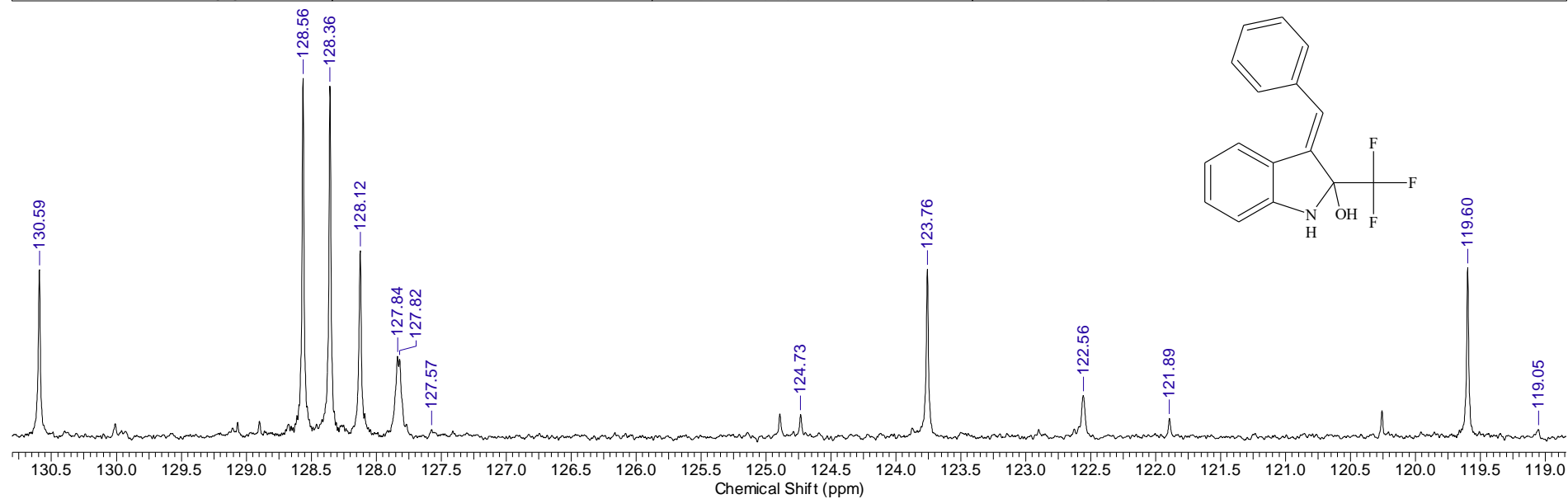
|                               |   |                             |                      |                              |                      |
|-------------------------------|---|-----------------------------|----------------------|------------------------------|----------------------|
| <b>Acquisition Time (sec)</b> | 4.0894  | <b>Comment</b>              | Imported from UXMNR. | <b>Date</b>                  | 22 Dec 2020 15:18:22 |
| <b>File Name</b>              | C:\DOCS\OUTPUT_301\2020\12_溴酚酮BM-2023-R.H_001001r | <b>Frequency (MHz)</b>      | 400.13               | <b>Points Count</b>          | 131072               |
| <b>Nucleus</b>                | <sup>1</sup> H                                    | <b>Number of Transients</b> | 4                    | <b>Original Points Count</b> | 32768                |
| <b>Pulse Sequence</b>         | zg30  | <b>Solvent</b>              | CHLOROFORM-D         | <b>Sweep Width (Hz)</b>      | 8012.82              |
| <b>Temperature (degree C)</b> | 27.000  |                             |                      |                              |                      |

<sup>1</sup>H NMR spectrum of **B** (400.1 MHz, CDCl<sub>3</sub>)

|                        |   |                      |                              |                       |                 |                        |        |
|------------------------|---|----------------------|------------------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 1.0000  | Comment              | STANDARD FLUORINE PARAMETERS |                       | Date            | Dec 18 2020            |        |
| File Name              | C:\DOCS\OUTPUT_301\F19\2020.12.18\BM-2023-R_20201218_01\FLUORINE_01 |                      |                              |                       | Frequency (MHz) | 376.31                 |        |
| Nucleus                | 19F   | Number of Transients | 16                           | Original Points Count | 89286           | Points Count           | 131072 |
| Pulse Sequence         | s2pul   | Solvent              | CHLOROFORM-D                 | Sweep Width (Hz)      | 89285.71        | Temperature (degree C) | 24.000 |

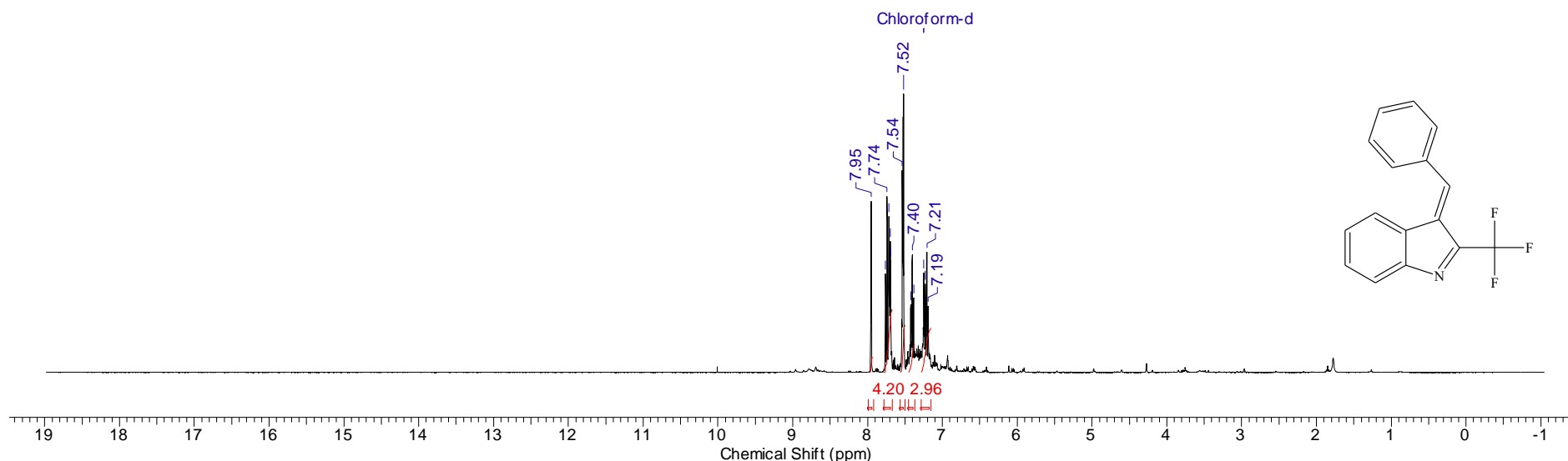
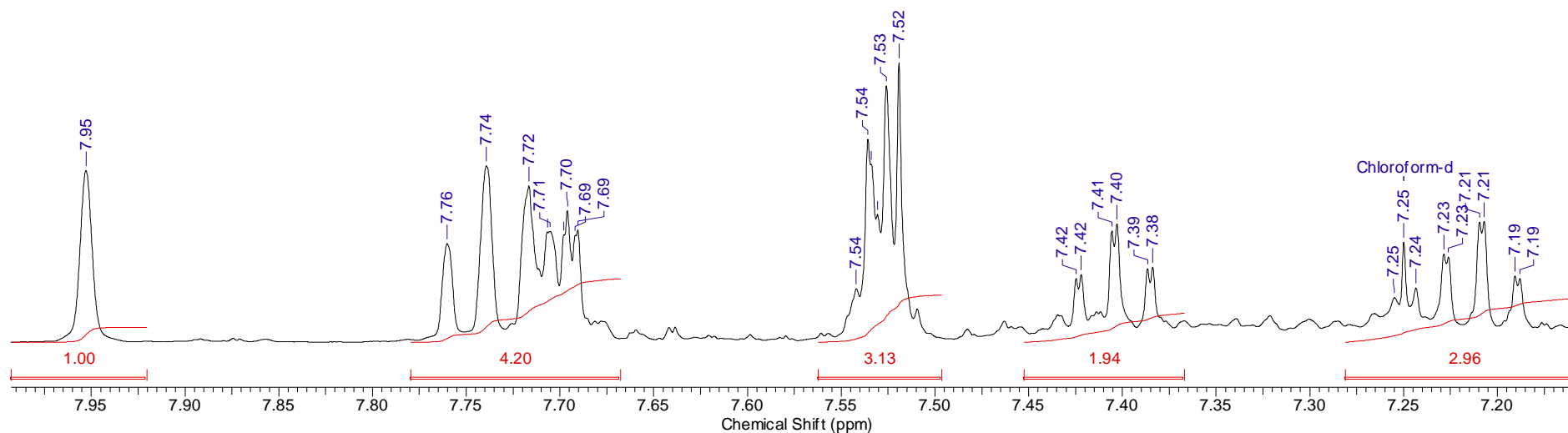
<sup>19</sup>F NMR spectrum of **B** (376.5 MHz, CDCl<sub>3</sub>)

|                        |   |                              |         |                       |                 |                        |        |
|------------------------|---|------------------------------|---------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 0.6783  | Comment Imported from UXMNR. |         |                       | Date            | 22 Dec 2020 15:27:46   |        |
| File Name              | C:\DOCS\OUTPUT_301\2020\12_溴脒衍BM-2023-R.C_002001r |                              |         |                       | Frequency (MHz) | 100.61                 |        |
| Nucleus                | 13C   | Number of Transients         | 233     | Original Points Count | 16384           | Points Count           | 131072 |
| Pulse Sequence         | zgpg30  | Solvent                      | DMSO-D6 | Sweep Width (Hz)      | 24154.59        | Temperature (degree C) | 27.000 |

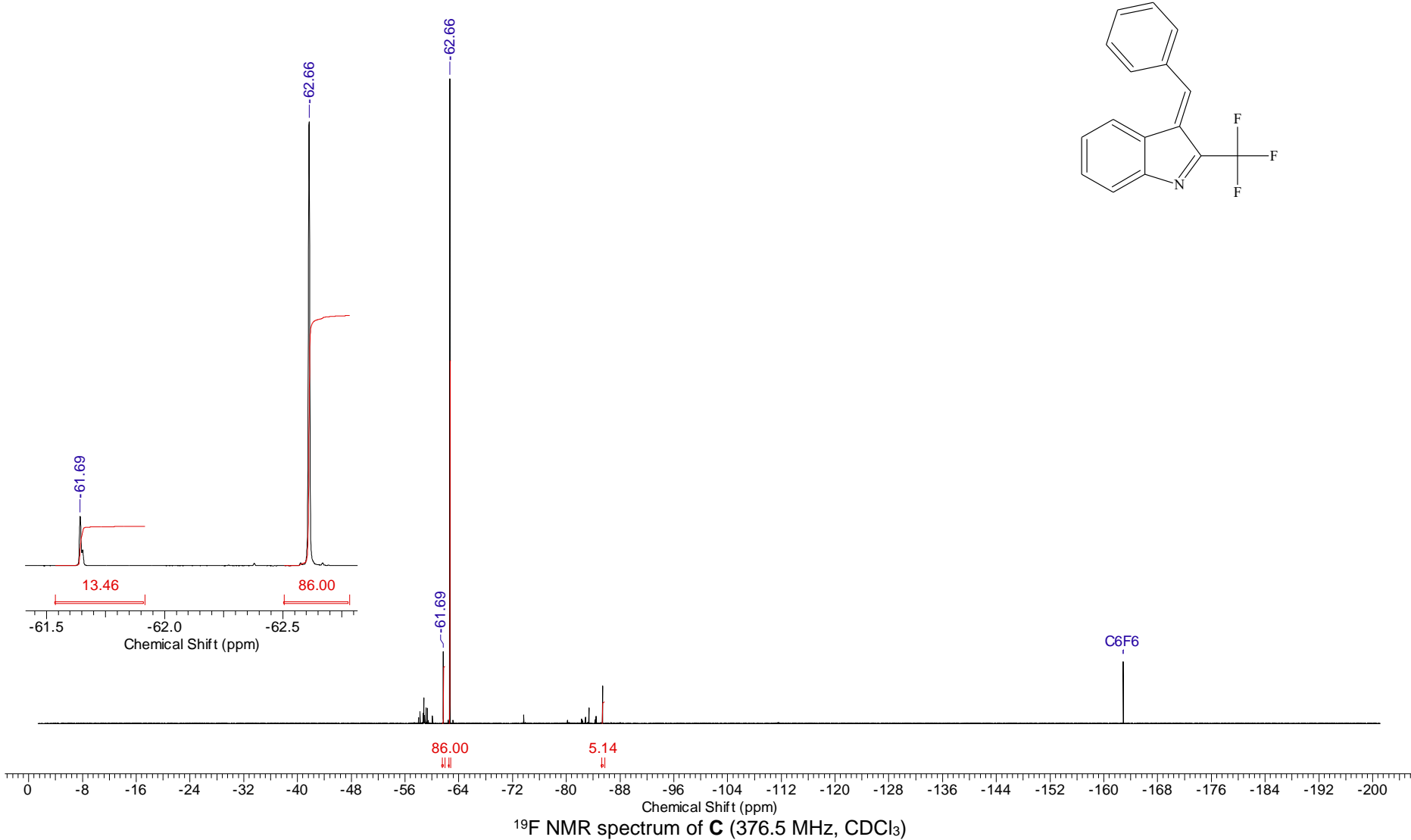
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **B** (100.6 MHz, CDCl<sub>3</sub>)



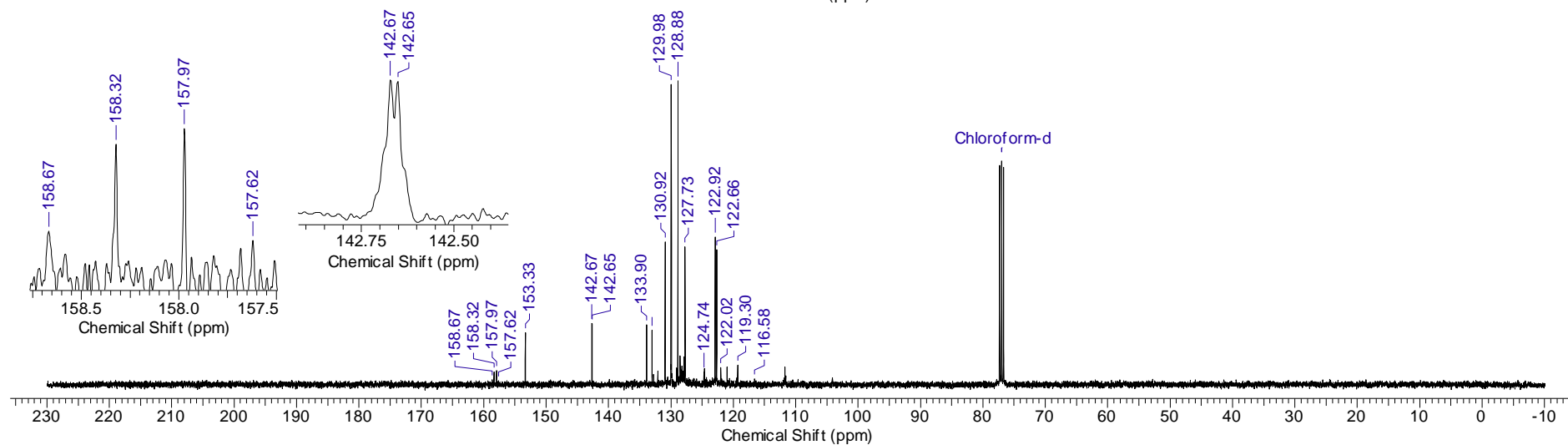
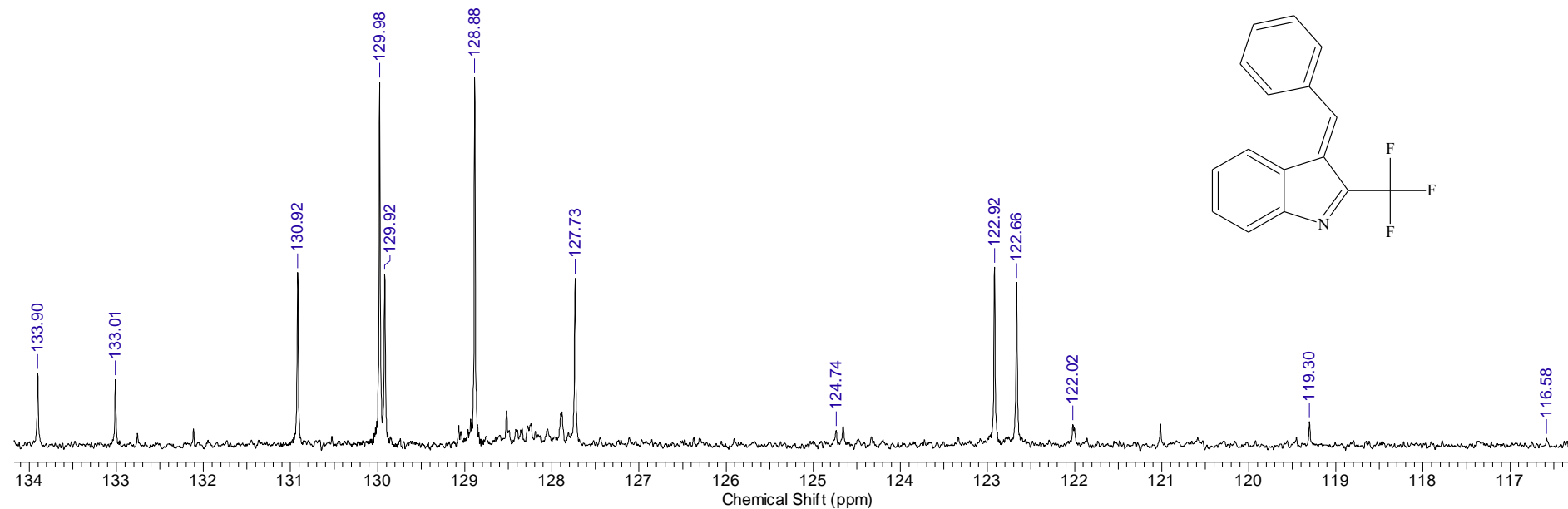
|                        |   |                      |                      |                       |                      |
|------------------------|---|----------------------|----------------------|-----------------------|----------------------|
| Acquisition Time (sec) | 4.0894  | Comment              | Imported from UXNMR. | Date                  | 27 Jan 2021 17:23:32 |
| File Name              | C:\DOCS\OUTPUT_301\2021\01. 微图黑BM-2023-R-21.H_001001r |                      |                      | Frequency (MHz)       | 400.13               |
| Nucleus                | <sup>1</sup> H  | Number of Transients | 4                    | Original Points Count | 32768                |
| Pulse Sequence         | zg30  | Solvent              | CHLOROFORM-D         | Points Count          | 131072               |
| Temperature (degree C) | 27.000  |                      |                      | Sweep Width (Hz)      | 8012.82              |

<sup>1</sup>H NMR spectrum of **C** (400.1 MHz, CDCl<sub>3</sub>)

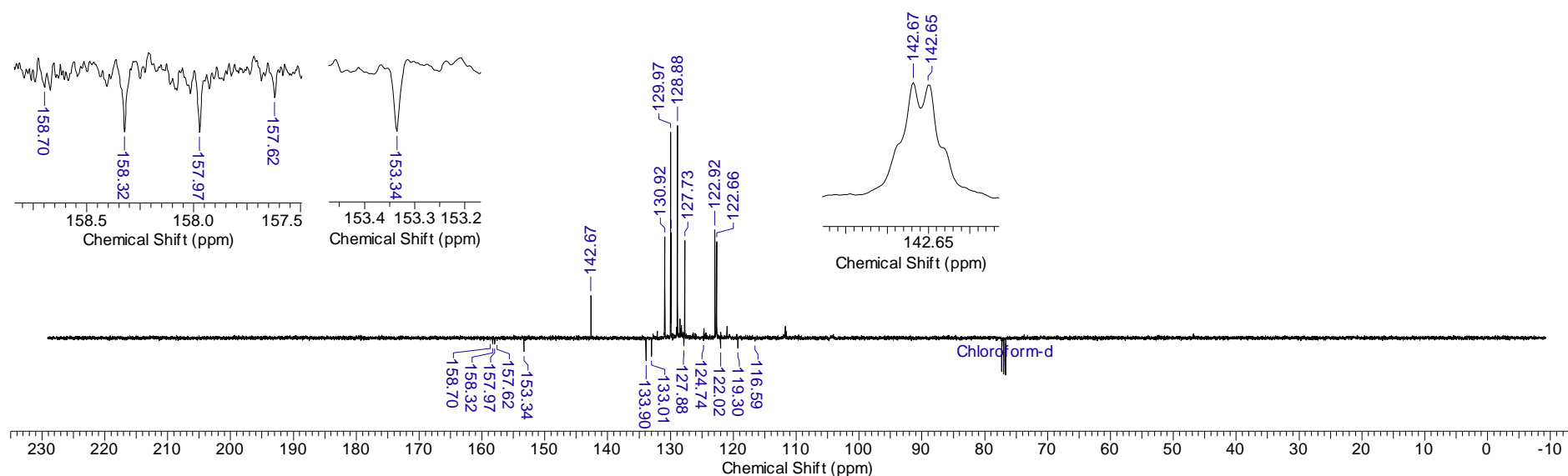
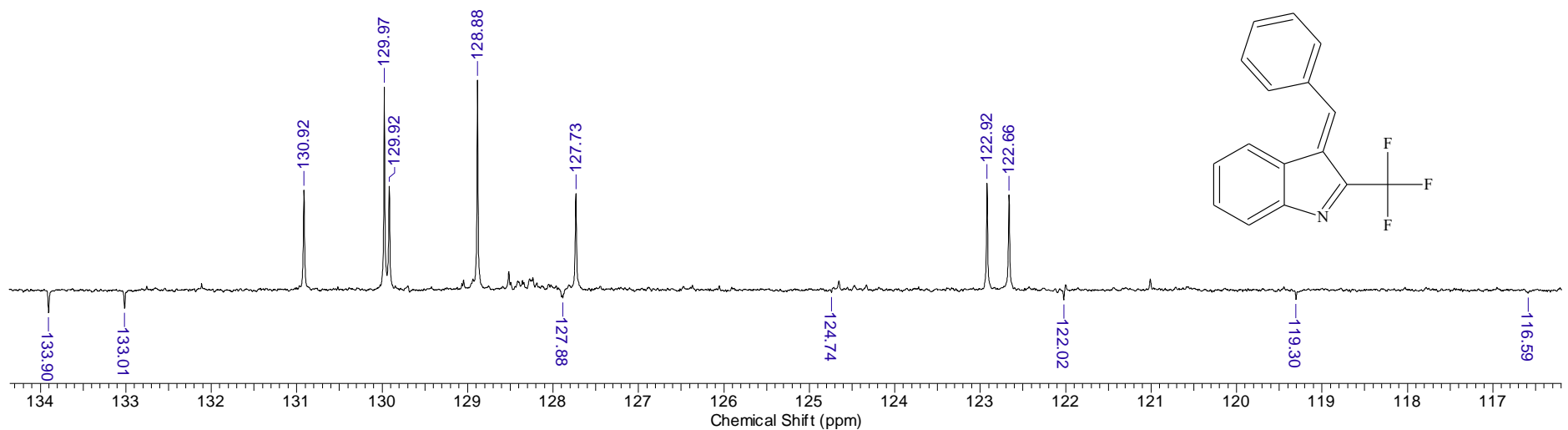
|                        |   |                      |                      |                       |                  |                      |        |
|------------------------|---|----------------------|----------------------|-----------------------|------------------|----------------------|--------|
| Acquisition Time (sec) | 1.7433  | Comment              | Imported from UXNMR. |                       | Date             | 26 Jan 2021 15:17:26 |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\01. 磁回黑BM-2023-R-21.F_005001r |                      |                      |                       | Frequency (MHz)  | 376.50               |        |
| Nucleus                | 19F   | Number of Transients | 16                   | Original Points Count | 131072           | Points Count         | 262144 |
| Pulse Sequence         | zgfgqn  | Solvent              | CHLOROFORM-D         |                       | Sweep Width (Hz) | 75187.97             |        |
| Temperature (degree C) | 27.000  |                      |                      |                       |                  |                      |        |



|                        |   |                      |                      |                       |                 |                        |        |
|------------------------|---|----------------------|----------------------|-----------------------|-----------------|------------------------|--------|
| Acquisition Time (sec) | 0.6783  | Comment              | Imported from UXNMR. |                       | Date            | 27 Jan 2021 17:35:28   |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\01. 微图黑BM-2023-R-21.C_002001r |                      |                      |                       | Frequency (MHz) | 100.61                 |        |
| Nucleus                | 13C   | Number of Transients | 241                  | Original Points Count | 16384           | Points Count           | 131072 |
| Pulse Sequence         | zgpg30  | Solvent              | DMSO-D6              | Sweep Width (Hz)      | 24154.59        | Temperature (degree C) | 27.000 |

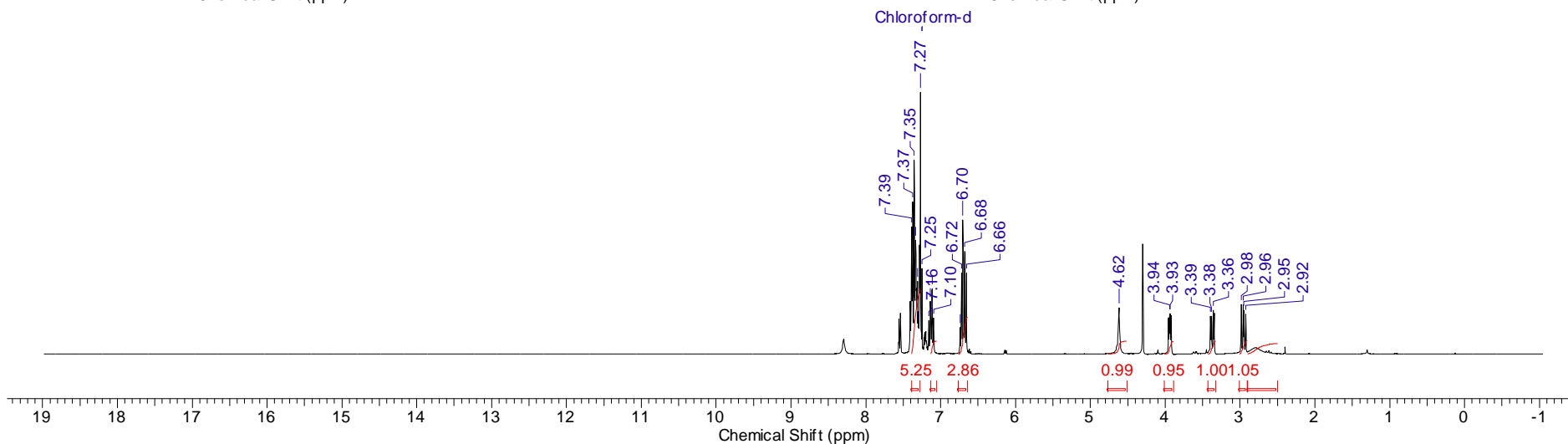
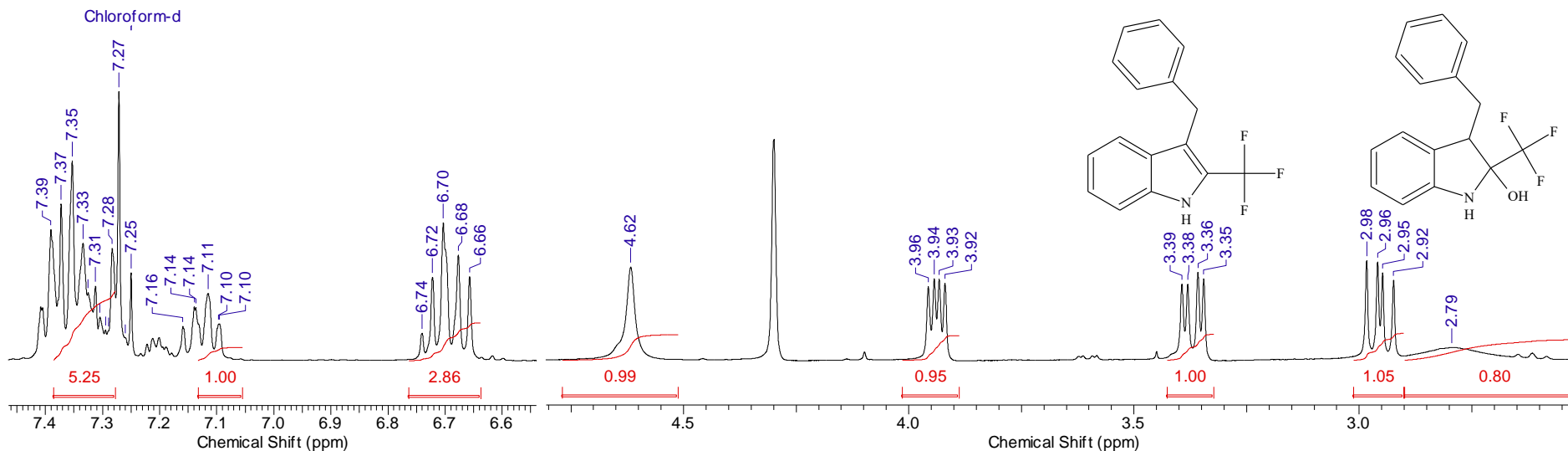
<sup>13</sup>C{<sup>1</sup>H} NMR spectrum of **C** (100.6 MHz, CDCl<sub>3</sub>)

|                        |   |                      |                      |                       |                  |                      |        |
|------------------------|---|----------------------|----------------------|-----------------------|------------------|----------------------|--------|
| Acquisition Time (sec) | 1.3664  | Comment              | Imported from UXNMR. |                       | Date             | 28 Jan 2021 12:18:36 |        |
| File Name              | C:\DOCS\OUTPUT_301\2021\01_ 微固黑BM-2023-R-21.APT_004001r |                      |                      |                       | Frequency (MHz)  | 100.61               |        |
| Nucleus                | <sup>13</sup> C   | Number of Transients | 109                  | Original Points Count | 32768            | Points Count         | 131072 |
| Pulse Sequence         | jmod  | Solvent              | CHLOROFORM-D         |                       | Sweep Width (Hz) | 23980.81             |        |
| Temperature (degree C) | 27.000  |                      |                      |                       |                  |                      |        |

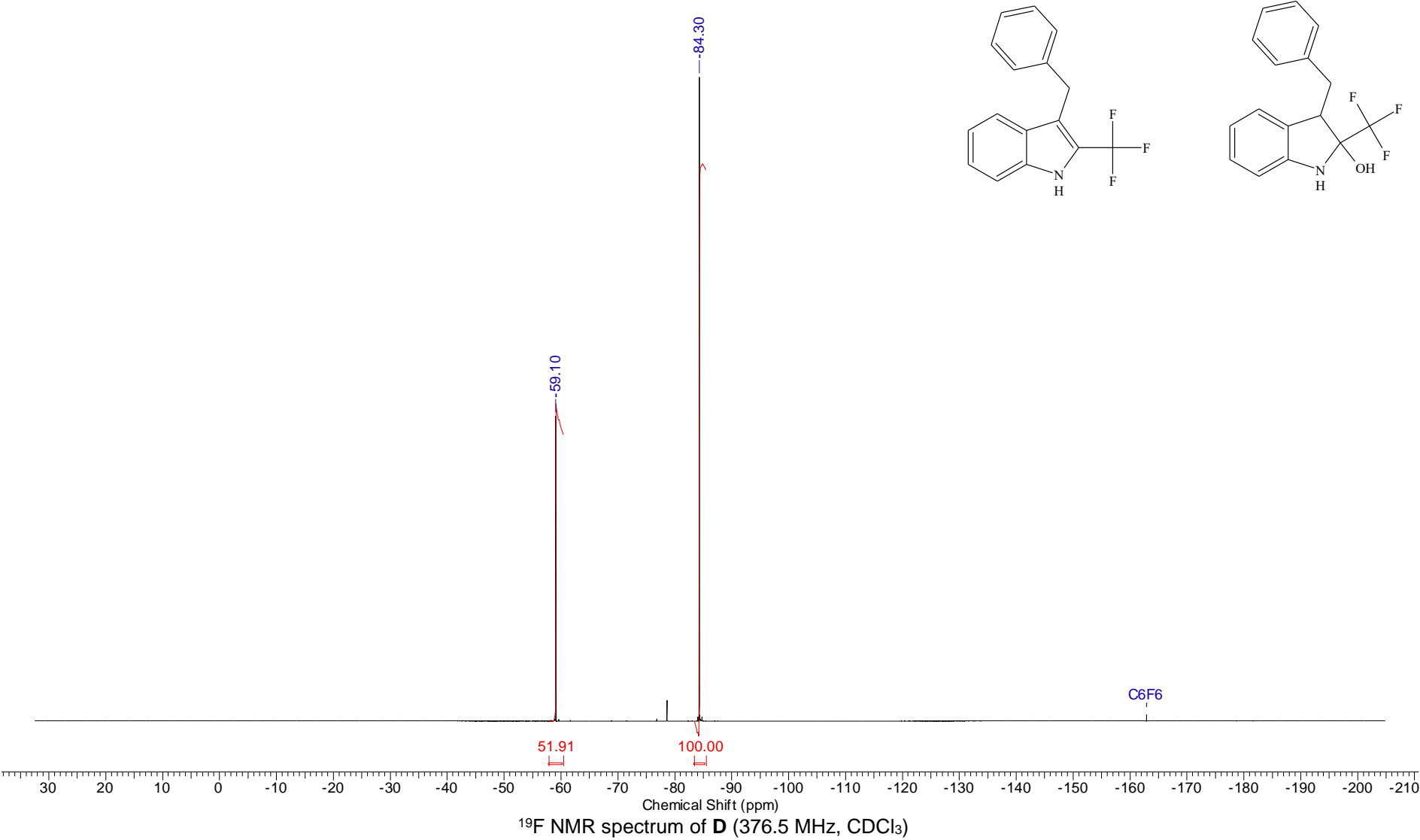
<sup>13</sup>C{<sup>1</sup>H} APT NMR spectrum of **C** (100.6 MHz, CDCl<sub>3</sub>)

|           |          |                |   |
|-----------|----------|----------------|---|
| <b>FW</b> | 568.5521 | <b>Formula</b> | C <sub>32</sub> H <sub>26</sub> F <sub>6</sub> N <sub>2</sub> O |
|-----------|----------|----------------|---|

|                        |   |                      |                      |                       |                  |                      |        |
|------------------------|---|----------------------|----------------------|-----------------------|------------------|----------------------|--------|
| Acquisition Time (sec) | 4.0894  | Comment              | Imported from UXMNR. |                       | Date             | 02 Dec 2019 15:59:26 |        |
| File Name              | C:\DOCS\OUTPUT_301\2019\12\溴赈粗品\BM-1816-R.H_001001r |                      |                      |                       |                  | Frequency (MHz)      | 400.13 |
| Nucleus                | 1H  | Number of Transients | 6                    | Original Points Count | 32768            | Points Count         | 131072 |
| Pulse Sequence         | zg30  | Solvent              | CHLOROFORM-D         |                       | Sweep Width (Hz) | 8012.82              |        |
| Temperature (degree C) | 27.000  |                      |                      |                       |                  |                      |        |

<sup>1</sup>H NMR spectrum of **D** (400.1 MHz, CDCl<sub>3</sub>)

|                               |          |                               |                       |                              |  |
|-------------------------------|----------|-------------------------------|-----------------------|------------------------------|--|
| <b>FW</b>                     | 568.5521 | <b>Formula</b>                | $C_{32}H_{26}F_6N_2O$ |                              |  |
| <b>Acquisition Time (sec)</b> | 0.7340   | <b>Date</b>                   | Dec 3 2019            | <b>File Name</b>             | C:\DOCS\OUTPUT_301\F19\2019.12.03\bm1816-r-f_20191203_01\FLUORINE_01 |
| <b>Frequency (MHz)</b>        | 376.31   | <b>Nucleus</b>                | $^{19}F$              | <b>Number of Transients</b>  | 100  |
| <b>Points Count</b>           | 65536    | <b>Pulse Sequence</b>         | s2pul                 | <b>Original Points Count</b> | 65536  |
| <b>Sweep Width (Hz)</b>       | 89285.71 | <b>Temperature (degree C)</b> | 22.000                | <b>Solvent</b>               | CHLOROFORM-D   |



Chemical structure of 2-(2-phenyl-2,2,2-trifluoroethyl)-1H-indole (19.98) is shown, along with its <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>). The spectrum displays peaks at 129.11, 128.70, 128.29, 26.68, and 124.80 ppm.

